

MEASUREMENT OF COAL DUST AND DIESEL EXHAUST AEROSOLS IN UNDERGROUND MINES

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ABSTRACT

In a cooperative study by the University of Minnesota and the U.S. Bureau of Mines, diesel exhaust and mineral dust concentrations have been measured for aerosols generated in the laboratory and in five underground coal mines. Three mines utilized diesel-powered haulage equipment and two used all-electric equipment. Two source apportionment techniques have been applied to differentiate between the mineral dust and diesel exhaust aerosol concentrations measured. The first technique, using a micro-orifice, uniform deposit impactor (MOUDI) for size selective sampling, is based on modeling aerosol size and the premise that the diesel exhaust portion of the aerosol is predominantly submicron and the mineral dust portion is mostly greater than one micrometer in size. The second technique, Chemical Mass Balance (CMB) modeling, was used to referee the analysis of diesel exhaust and mineral dust aerosol concentrations from the size selective sampling results.

The MOUDI size distribution data were modeled to obtain parameters describing the fine and coarse fractions of the sampled aerosol and to estimate the contributions to each mode from both mineral dust and diesel exhaust aerosol sources. The results showed the size distribution of the mixed aerosols exhibited two definite modes with the minimum between the modes occurring at 0.8 μm . Less than 5 pct of the coal mine diesel aerosol was found in the coarse size fraction. CMB analysis confirms the original premise for using aerosol size to separate diesel exhaust and mineral dust aerosol during sampling.

Based on the results from the size selective sampling, a personal diesel aerosol sampler has been developed for measuring diesel aerosol mass concentrations. This sampler uses an inertial impactor to size separate the respirable aerosol at 0.8 μm . All material less than 0.8 μm is collected on an afterfilter for subsequent gravimetric analysis.

INTRODUCTION

Measurement of the contribution of diesel exhaust to respirable aerosol in mine environments has become increasingly important because of recent research which suggests that exposure to diesel exhaust particulate matter may have adverse occupational health effects. To support these efforts, the U.S. Bureau of Mines is developing and evaluating new sampling methods for the measurement of diesel aerosol in underground coal mines.

Two of these techniques are size selective sampling and chemical mass balance modeling (CMB). Size selective sampling, is being adapted for diesel aerosol sampling by the Particle Technology Laboratory (PTL) of the University of Minnesota under sponsorship by the.¹ It is based on the premise that diesel and mineral dust aerosol can be physically separated by size and collected during sampling using inertial impaction.

The second technique, CMB, is an alternative measurement technique used to referee the results obtained using size selective sampling.² It compares elemental 'finger prints' of the aerosol sources with similar profiles measured for mine aerosol samples. From this the portions of the sample contributed by each source can be determined.

The Bureau and the PTL have conducted a study in five coal mines using both size selective sampling and the CMB techniques. This study was undertaken as a follow-on to the laboratory study of size selective sampling applied to the measurement of diesel aerosol.¹ The results from the laboratory and field studies are summarized in this paper. The design of a prototype personal diesel aerosol sampler, based on the size selective results, is also presented.

LABORATORY EXPERIMENT

Laboratory experiments were conducted to investigate the

feasibility of using the Micro-Orifice, Uniform Deposit Impactor (MOUDI) to measure the size distribution of aerosols containing various mixtures of coal dust and diesel exhaust aerosols.¹ The objective of the work was to determine the mass concentration of diesel exhaust aerosol in an airborne mixture of coal dust and diesel exhaust aerosol from the size distribution of the mixed aerosol. A prototype seven stage MOUDI with cut sizes ranging from 0.1 to 10 μm was used.³

The experiment successfully demonstrated that coal dust and diesel exhaust aerosol can be separated and measured on the basis of size. Data from the tests, typified in Figure 1, show that the overall diesel exhaust/coal aerosol size distribution is bimodal with the diesel exhaust (accumulation) mode aerosol having a mass median aerodynamic diameter (MMD) of approximately 0.15 μm . The coal (coarse particle) mode has a MMD in the 3 to 10 μm size range. A clear separation between the two modes exists in the 0.7 to 1.0 μm size range with the minimum near 0.8 μm . Analysis of a combined size distribution permits a quantitative determination of the diesel aerosol contribution to within 15%.

FIELD STUDIES

The five mines visited during the field study are summarized in Table I. The table indicates each mine's geographical region, coal type being mined, and type of haulage equipment used. Three of the mines, A, B, and H were equipped with diesel haulage equipment and C and G had all electric equipment. The electric equipped coal mines were used to generate comparison samples for a mine environment without diesel aerosol.

Measurements consisted of collecting size differentiated aerosol samples at four locations in longwall development sections employing a continuous miner: in the air intake entry, conveyor beltway entry, air return entry, and haulage way. A ten stage MOUDI was used for most of the field size distribution measurements and a dichotomous sampler was used to collect aerosol for the elemental analysis used in the CMB model calculations. The samplers and CMB analysis are described elsewhere.^{2,4} Both samplers were operated at a flow rate of 30 lpm.

Aerosol samples were collected at the intake and haulage or beltway locations periodically during each mine work shift. Sampling at the return location was usually conducted only once during the shift, while the continuous miner was in operation. Samples of primary interest were those collected at the conveyor belt or in the haulage way since they are from areas where workers are exposed. These were collected only when the breaker was on and diesel haulage equipment was in use. As a result, no attempt was made during the field experiments to take representative exposure samples for the work shift. The focus of the study was on developing a method for measuring the diesel component of a mine aerosol containing a mixture of both diesel exhaust particulate and mineral dust.

Trace element profiles of mine aerosol sources used in the CMB analysis were obtained from samples of the material from which the diesel or mineral dust aerosols originate.

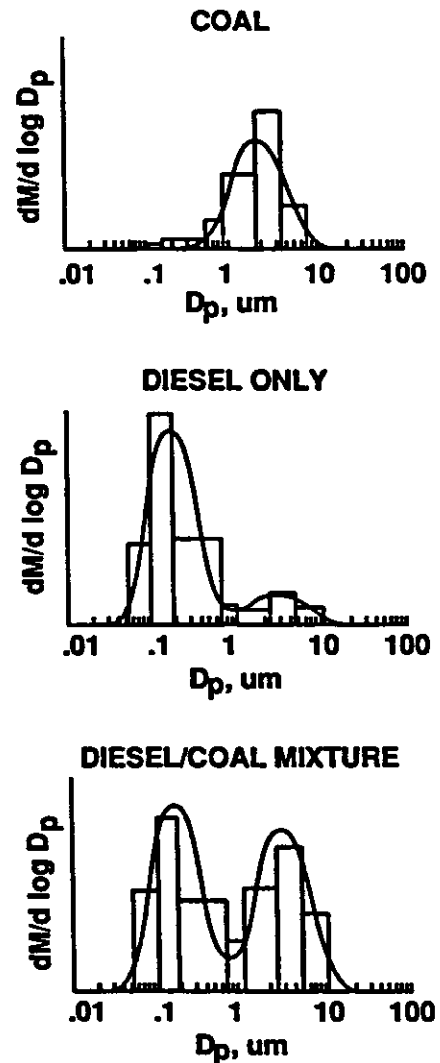


Figure 1. Laboratory diesel/coal dust size distributions.

Bulk material samples were collected of coal and the rock dust used in the mine as an explosion and fire retardant. For the diesel equipped mines visited, exhaust source aerosol samples were collected from the tailpipes of the haulage vehicles operating in the mine. In each case, the assumption is made that the profiles thus obtained are representative of the aerosols originating from these sources.

Where collection of diesel tailpipe aerosol samples was not feasible, diesel fuel and diesel lubricating oil were collected to use as a surrogate for the diesel exhaust aerosol source.⁵ To enhance the use of diesel fuel as a surrogate for diesel aerosol emissions, a tracer material, a nominal 10 parts per billion of Indium as Indium 2,4 pentanedionate in xylene, was added to the fuel supply for the vehicles operating in the test section of the mines. The trace element analysis technique used Instrumental Neutron Activation Analysis (INAA), was performed by the University of Rhode Island.⁶

FIELD MEASUREMENT RESULTS

Average aerosol size distributions measured in the haulage

Table I
Mine Data for Operations Visited FY 85-87

Mine	Region	Haulage	Coal Rank
A	West	Diesel	HVB* C ¹
B	West	Diesel	HVB C ²
C	East	Electric	HVB B ¹
G	East	Electric	HVB A ³
H	Midwest	Diesel	HVB B ³

* HVB - High Volatile Bituminous

Sources

¹ Based on ASTM Standards.

² Company information

³ 1987 Keystone Coal Industry Manual. McGraw-Hill, Inc., New York, 1987, 1244 pp.

way of the diesel equipped and all-electric coal mines are shown in Figures 2 and 3. The MOUDI separates and collects the sampled aerosol in several size intervals by aerodynamic diameter. The number of size intervals provides enough differential size resolution to model the measured aerosol size distributions with empirical functions. This analysis, termed modal analysis, uses a sum of two log-normal functions to fit the data.⁷ Each function represents one of the maxima or modes evident in the data. The log-normal distribution parameters, given in Table II for the average distributions, are the mass mean diameter (MMD), geometric standard deviation (σ_g) and mode concentrations.

Each mode can be identified with the aerosol contributed by a primary aerosol source; diesel exhaust aerosol for the sub-micron mode and mineral dust for the coarse particle mode. Under this assumption, the separate contributions from these sources to the total aerosol concentration can be determined using modal analysis. Treating each mode as a source connected entity, also permits the determination of that portion of the coarse particle mode that encroaches on a sample of submicron mode aerosol as it might be collected by a size selective sampler. This is done by integrating the distribution function for the coarse particle mode over the range of sizes for which the submicron mode aerosol is collected. An illustration of such modal overlap for the average diesel/coal size distribution of Figure 2 is given in Figure 4. The range of integration is 0.001 to 0.8 μm . Shaded areas indicate the portion of the submicron and coarse aerosol that will contribute to a sub-0.8 μm sample.

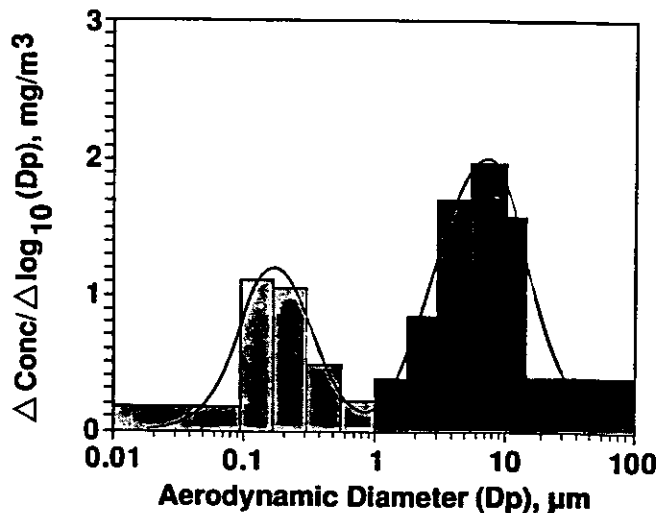


Figure 2. Average mass size distribution measured in the haulage entries of diesel equipped coal mines.

A comparison between modal and CMB analysis results is given in Table III. Values from the modal analysis for the fraction of sub-0.7 μm aerosol contributed by the coarse particle mode are $7 \pm 5\%$ for mine A, $15 \pm 7\%$ mine B, and less than 2% for mine H. Results for mine A and H are well within each others stated variability. There is a barely resolvable difference between the two analysis results for

Table II
Summary of Log-normal Size Distribution Parameters for Average Aerosol Distributions
Measured in Haulage Entries of Diesel Equipped and All-electric Coal Mines

Mine Type	Submicron			Coarse		
	Mass Mean Dia. ¹ um	Geometric Std. Dev. ²	Mode ³ Conc. mg/m ³	Mass Mean Dia. um	Geometric Std. Dev.	Mode Conc. mg/m ³
Diesel	0.17±0.04	2.0±0.3	0.88±0.52	6.8±1.6	2.3±0.3	1.8±0.8
Electric	0.46±0.10	2.6±0.9	0.06±0.04	7.2±2.0	2.0±0.3	1.2±0.8

¹ Mass Mean Diameter (MMD)

² Geometric Standard Deviation (σ_g)

³ Mode Concentration

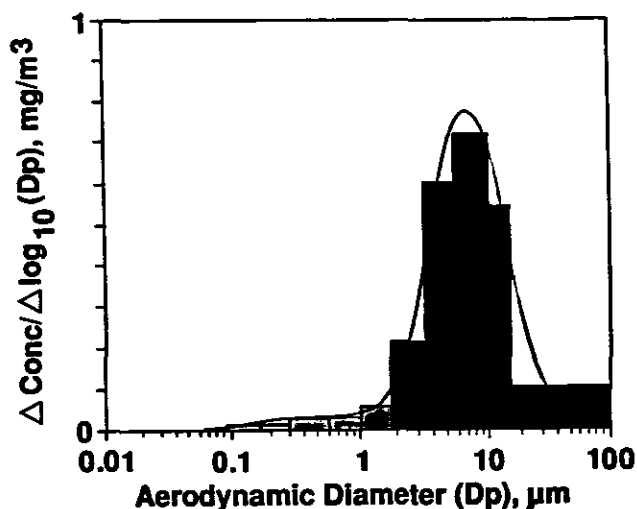


Figure 3. Average mass size distribution measured in the haulage entries of all-electric equipped coal mines.

mine B. This difference may be due to the limited number of samples analyzed.

Using the results of the limited CMB analysis, two key points can be made concerning the contribution of the various diesel mine sources to fine and coarse aerosols in the mine environment. These are:

1. Diesel emissions aerosol is the dominant component of the submicron mode aerosol measured in the diesel mines. From 75 to 90% of the measured aerosol concentration is contributed from diesel sources.
2. Coal is the primary component of the coarse aerosol, as much as 92%.

Table III
Average Coarse Particle Contamination of Sub-0.7 μm
Samples for Mines A, B and H

Mine	Analysis	
	Modal %	CMB %
A	7±5	<8
B	15±7	25±4
H	<0.2	<4

These points confirm the basic assumptions advanced to justify the use of the MOUDI or other size selective sampler to separate and measure diesel and mineral dust aerosol in the mine environment. Separate confirmation for the assumption that the mineral aerosol contributes predominantly in the coarse aerosol size range is found in the average size distribution measurement results for the all-electric equipped coal mines in Figure 3.

The optimum particle size for the separation of diesel from mineral dust aerosol was determined from the average size distribution measured in the haulage entries of the three mines using diesel equipment. This analysis treated the submicron mode as entirely diesel aerosol and the coarse particle mode as entirely mineral. Integrating the log-normal functions that describe the size distribution modes from zero up to a given size, as illustrated in Figure 4, the aerosol mass that would be collected by a sampler with that separation size was determined. Using these results, the gravimetric error made by assigning the aerosol mass collected by the sampler to diesel aerosol alone was calculated as a function of separation size. The least error, ±7%, occurs for size separation at 0.8 μm.

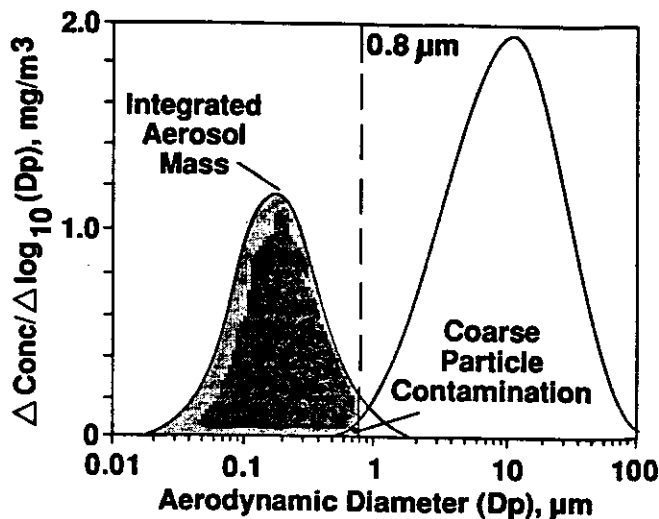


Figure 4. Illustration of the integration of aerosol mode functions to calculate aerosol mass less than $0.8 \mu\text{m}$.

PERSONAL DIESEL AEROSOL SAMPLER

A prototype personal diesel exhaust aerosol sampler has been designed for underground coal mines. The sampler was designed on the premise that size selective sampling techniques can be used to separate diesel exhaust aerosol, which is predominantly submicron in size, from coal dust aerosol, which is mostly greater than a micron in size. The sampler has three stages and employs inertial impaction for particle separation. The first, sample inlet/preclassifier, stage is a composite impactor with an aerosol penetration efficiency that conforms to either the American Conference of Industrial Hygienists (ACGIH) or the British Medical Research Council (BMRC) respirable dust sampling criteria. This first stage serves as a preclassifier to select the respirable portion of the sample aerosol and prevent overloading of the second stage. The second stage is a multiple-orifice impactor with a sharp separation or cut size that passes only aerosol smaller than $0.8 \mu\text{m}$. The respirable aerosol larger than $0.8 \mu\text{m}$ is deposited on an impaction plate. The third stage, which is a filter, collects all aerosol less than $0.8 \mu\text{m}$ aerodynamic diameter. This instrument is a research prototype and the design permits the second stage impaction substrate to be removed for gravimetric and chemical analysis. To increase the amount of sample for such analysis, the sample flow rate for the prototype will be 4 lpm. The sampler can be modified for the DORR-OLIVER 10 mm cyclone preclassifier and a flow rate of 2 lpm.

A schematic diagram of the sampler is presented in Figure 5. The sampler inlet is a 2.5 cm. ring of nozzles in the sampler cover. These nozzles are part of a preclassifier/impactor with an aerosol collection efficiency that can approximate either the ACGIH or the BMRC respirable dust sampling criteria.⁸ The impaction surface for this first section is a porous plate impregnated with oil to reduce particle bounce and blow off. A sample stream next passes to a multiple-orifice impactor with a cutpoint of $0.8 \mu\text{m}$. The impaction plate for this stage is a removable aluminum foil

coated with silicone oil. The sample stream then passes through a filter which removes the remaining aerosol. Sampler height is 2.5 cm. The sampler divides the respirable aerosol into two size fractions, greater and less than $0.8 \mu\text{m}$. These samples can be used to measure the concentrations of the diesel and mineral dust portions of respirable coal mine aerosol.

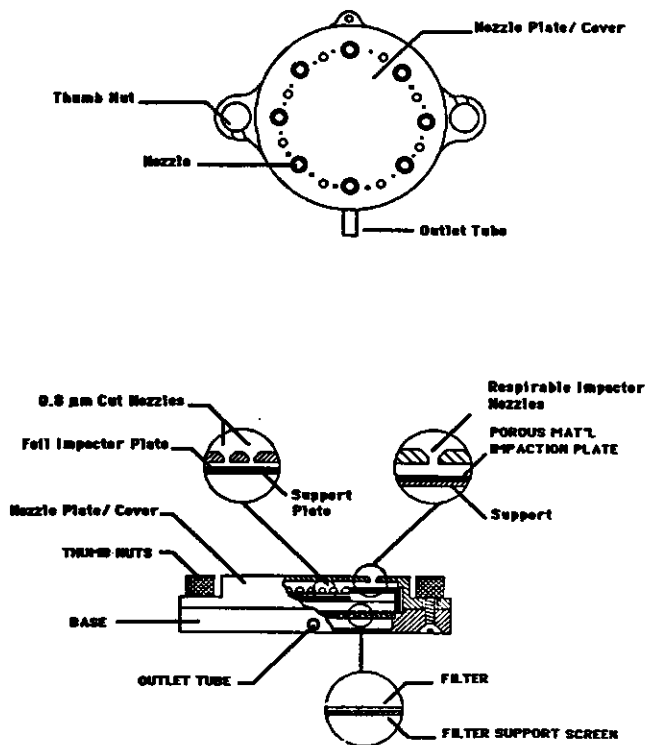


Figure 5. Schematic diagram of personal respirable/diesel aerosol impactor sampler.

The primary limitations on a personal diesel sampler based on size selective sampling are diesel aerosol loss from the sample, contamination by coarse particle mode aerosol, and resolution of the gravimetric analysis performed on the sample. Of secondary importance is the presence of background aerosol in the sample. The latter is due to external diesel, atmospheric, or nondiesel sources of submicron aerosol. The final sample contains most of the diesel particulate material present in the mine air plus a small amount of mineral dust, usually less than 10%. If a sample flow rate of 2 lpm is used and gravimetric analysis is to within 0.1 mg, a sub- $0.8 \mu\text{m}$ aerosol concentration should have a limit of detection of 0.3 mg/m^3 .

CONCLUSIONS

The primary result from this study is that size selective sampling can be effective as a technique for measuring diesel aerosol concentrations in underground coal mines. The MOUDI size distribution data were modeled to obtain parameters describing the fine and coarse fractions of the sampled aerosol and to estimate the contributions to each mode from both mineral dust and diesel exhaust aerosol

sources. The results showed the size distribution of the mixed aerosols exhibited two definite modes with the minimum between the modes occurring at 0.8 μm . CMB analysis confirms the original premise for using aerosol size to separate diesel exhaust and mineral dust aerosol during sampling.

A personal diesel aerosol sampler has been developed for measuring the diesel aerosol concentration in underground coal mines. This device consists of three sequential stages. The first stage classifies aerosol in the sample stream according to the BMRC respirable efficiency curve. The second stage separates the resulting respirable aerosol into two parts by aerodynamic diameter using a single stage impactor with a cutpoint of 0.8 μm . The third stage collects the <0.8 μm diameter aerosol on a media that is suitable for gravimetric analysis.

REFERENCES

1. Marple, V.A., Kittelson, D.B., Rubow, K.L. and Fang, C.P.: *Methods for the Selective Sampling of Diesel Particulate in Mine Dust Aerosols*. BuMines OFR 44-87, NTIS PB88-130810, Washington (1986).
2. Cantrell, B.K.: Source Apportionment Analysis Applied to Mine Dust Aerosols: Coal Dust and Diesel Emissions Aerosol Measurement. *Proc. 3rd Mine Vent Symp.*, pp.495-501. Soc. Mining Eng., State College, PA, (1987).
3. Marple, V.A. and Rubow, K.L.: *Development of a Micro-Orifice Uniform Deposit Impactor*. U.S. Dept. of Energy, No. DOE/PC/61255, Wash. D.C. (1984).
4. Cantrell, B.K. and Rubow, K.L.: Mineral Dust and Diesel Aerosol Measurements in Underground Metal and Non-metal Mines. *Proceedings of the VIIth International Pneumoconioses Conf. National Institute for Occupational Safety and Health et. al.*, Pittsburgh, PA (1988).
5. Pierson, W.R. and Brachaczek, W.W.: Particulate Matter Associated with Vehicles on the Road. II. *Aerosol Sci. and Tech.*, 2:1-20 (1983).
6. Rahn, K.A.: *The Chemical Composition of the Atmospheric Aerosol*. University of Rhode Island, Tech. Rpt, Narragansett, RI, (1976).
7. Whitby, K.T. *Modeling of Atmospheric Aerosol Particle Size Distributions*. U.S. EPA Grant Rpt, No. R800971, (1975).
8. Marple, V.A. and McCormack, J.E.: Personal Sampling Impactor with Respirable Aerosol Penetration Characteristics. *Am. Ind. Hyg. Assoc. J.*, 44:916-922 (1983).

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MINERAL DUST AND DIESEL EXHAUST AEROSOL MEASUREMENTS IN UNDERGROUND METAL AND NONMETAL MINES

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INTRODUCTION

Measurement of the contribution of diesel exhaust to respirable aerosol in mine environments has become increasingly important because of current concerns over the occupational health effects resulting from exposure to diesel emissions. In response to this, the U.S. Bureau of Mines is developing and evaluating new sampling methods for measuring diesel aerosol in underground mines. Two such techniques are being studied by the Bureau, size selective sampling and Chemical Mass Balance (CMB) modeling. These techniques use measurable physical or chemical characteristics of a mine aerosol sample to infer the amount of diesel particulate material contained in the sample.

Size selective sampling is being adapted for measurement of diesel aerosol by the Particle Technology Laboratory (PTL) of the University of Minnesota under sponsorship by the Bureau.¹ It is based on the premise that diesel and mineral dust aerosol can be physically separated by size and collected during sampling using inertial impaction. An independent effort by the National Institute for Occupational Safety and Health to develop a size selective sampling technique was also sponsored by the Bureau.²

The second technique, CMB modeling, is being developed by the Bureau as an alternative measurement technique to referee the results obtained using size selective sampling.³ It compares measured trace element "finger prints" of aerosol sources with similar profiles of mine aerosol samples. From these, the portions of the sample contributed by each source can be determined. Results of these investigations in underground coal mines have confirmed that diesel and coal dust aerosol are of different size and can be measured separately using size selective sampling techniques.⁴

A major difference in diesel usage among underground mines is the requirement for exhaust gas cooling systems in coal and gassy noncoal mines. Nongassy mines usually employ limited exhaust conditioning in the form of catalytic converters, which have limited effect on primary exhaust particulate. The cooling system in most general use in gassy mines is the water scrubber. This device has little effect on most of the gases but removes particulate material from the exhaust.⁵ Because of this, exhaust aerosol characteristics in nongassy mines are expected to be different. To see if size

selective sampling techniques can be used in such mines, the Bureau and the University of Minnesota conducted a second study in three metal and nonmetal mines, two nongassy and one rated as gassy.

FIELD STUDIES

The field study conducted in metal and nonmetal mines is summarized in Table I. The table indicates each mine's geographical region, the material being mined, and the type of haulage equipment used. The studies consisted of collecting size-differentiated aerosol samples at four locations in a working section employing diesel haulage equipment: the air intake entry (I), beltway entry—where applicable (B), air return entry (R), and haulage way (H). These locations are illustrated in Figure 1 for the soda ash mine.

Aerosol samples were collected using Micro-Orifice, Uniform Deposit Impactor (MOUDI) and respirable dichotomous samplers.⁴ The MOUDI, used for size distribution measurements, is a 10-stage cascade impactor with particle separation sizes at 15, 10, 5.62, 3.16, 1.78, 1.0, 0.562, 0.316, 0.178, and 0.1 μm plus an after-filter. The dichotomous sampler was used to collect aerosol for the elemental analysis used in the CMB model calculations. It consists of an impaction-type inlet designed to pass sample aerosol with an efficiency approximating the American Conference of Governmental Industrial Hygienists (ACGIH) respirable dust sampling criteria, followed by two MOUDI impaction stages, both with 0.7- μm separation sizes, plus an after-filter.⁶ Configured in this way, the dichotomous sampler provides a partition of the collected respirable aerosol sample into two size fractions, greater and less than 0.7 μm in size. This partition was selected because it was close to the size found to separate diesel exhaust and coal dust aerosol components in laboratory studies and the impactor stages were available.¹ Both samplers operate with a 30 lpm sample flow rate.

Trace element profiles of mine aerosol sources used in the CMB analysis were obtained from samples of the material from which the diesel or mineral dust aerosols originate. Exhaust source aerosol samples were collected from the tailpipes of the haulage vehicles operating in the mine. Bulk material samples were collected of the mineral being mined. In each

Table I
Mine Data for Metal/Nonmetal Mines Visited 1985-1987

Mine	Region	Haulage	Type of Material
D	Midwest	Diesel	Shale
E	West	Diesel*	Soda Ash
F	West	Diesel	Quartzite

*Gassy mine, water scrubbers used on diesel equipment.

SAMPLING SITE LOCATIONS

- H** - Haulage Way Site
- R** - Return Site
- I** - Intake Site
- B** - Breaker Site
- - Ventilation Pathway
- C-X** - Working Face
- II** - Stopping
- III** - Stopping + Man Door

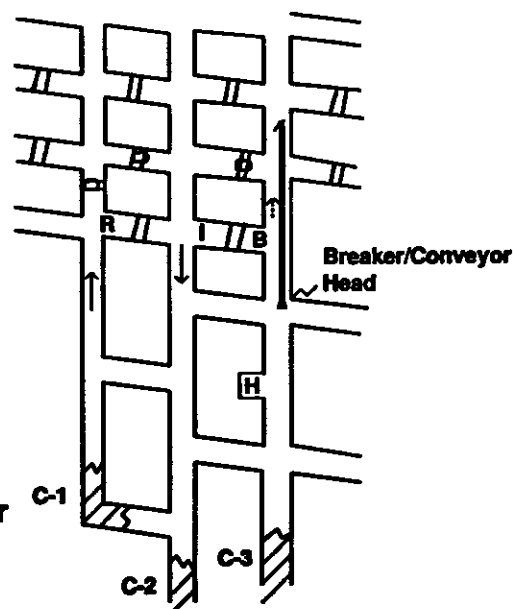


Figure 1. Sampling site locations used for in-mine sampling experiments are indicated together with ventilation vectors.

case, the profiles obtained are assumed to be representative of the aerosols originating from these sources.

To enhance the diesel tailpipe samples, a tracer material, a nominal 10 parts per billion of indium as indium 2,4 pentanedionate in xylene, was added to the fuel supply for the vehicles operating in the test section of the mines. The trace element analysis technique used, instrumental neutron activation analysis (INAA), is very sensitive to indium, which is rarely found in nature.⁷

Aerosol samples at haulage way or beltway locations were collected periodically during the entire mine work shift. Since they were collected in areas where workers are exposed, they are the samples of primary interest. Sample collection was only done when the conveyor belt was on and diesel haulage equipment was in use. The samples collected are therefore biased toward high concentrations of both diesel and mineral aerosol and are not representative personal exposure samples for the work shift. Although not analyzed for the study, sampling at the return location was conducted once during the shift, while the continuous miner was in operation.

Measurement and Analysis Techniques

Only two measurement techniques were used in the field study. These were gravimetric analysis of the impaction substrates and after-filters from both the MOUDI and dichotomous samplers and elemental analysis of the dichotomous samples using INAA.³

INAA was performed at the University of Rhode Island.⁸ Analyses were performed on dichotomous substrates and after-filter pairs containing sufficient aerosol mass for irradiation (1 mg or more), quality control blanks of both substrate and after-filter, and samples of the aerosol source materials. The source materials were analyzed in triplicate, and average values for the resulting element concentrations were used in the CMB analysis.

Modal Analysis

Average aerosol size distributions measured in the haulage way of the diesel-equipped mines visited are shown in Figure 2. The measured aerosol size distributions were modeled using a sum of two log-normal functions to fit the data.⁹ Each

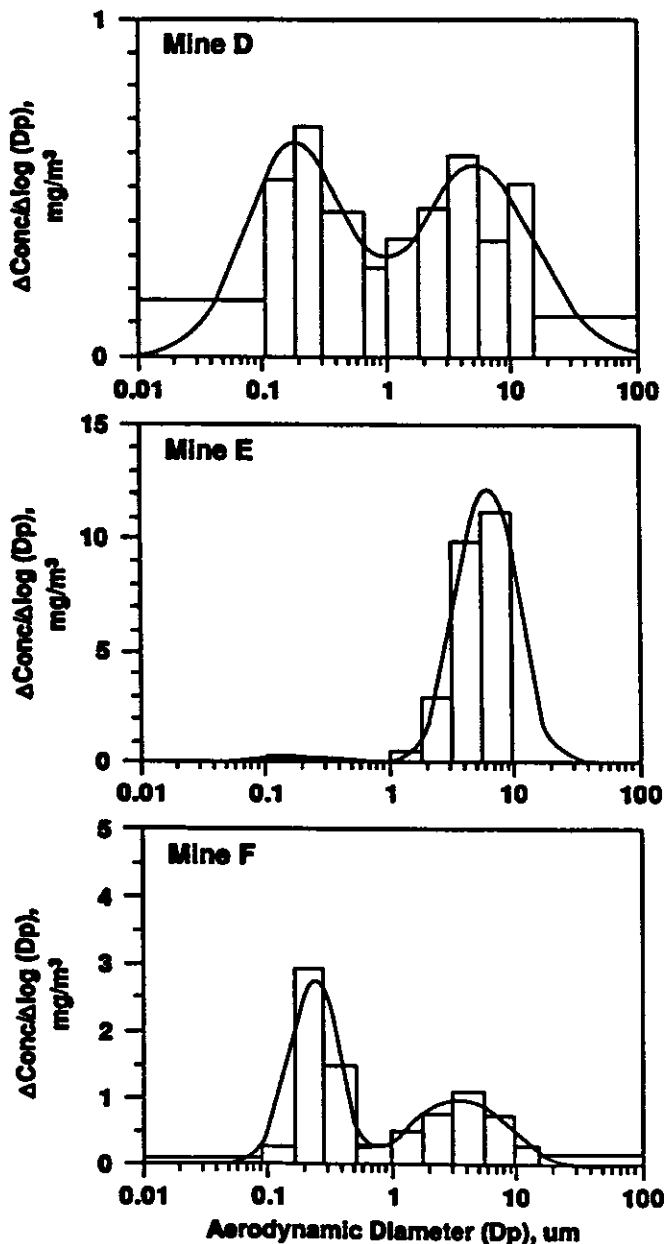


Figure 2. Average mass size distribution measured in the haulage entries of mines D, E, and F.

function represents one of the maxima, or modes, evident in the data. The log-normal distribution parameters, given in Table II for the average distributions, are the mass mean diameter (MMD), geometric standard deviation (σ_g), and mode concentrations.

For coal mines, each mode was identified with the aerosol contributed by a primary aerosol source diesel exhaust aerosol for the submicron mode and mineral dust for the coarse particle mode.³ Under this assumption, the separate contributions from these sources to the total aerosol concentration can be determined using modal analysis. For these noncoal mines, the results of the size measurements are very

similar. Two well-separated aerosol modes are evident for each of the mines. It remains for the CMB analysis to determine whether the same interpretation can be made.

CMB Model Analysis

CMB model analysis permits the relating of elements or chemical components in an aerosol sample collected at a given location to those same components in the sources of the aerosol.^{10,11} The model is expressed as:

$$C_i = \sum_{j=1}^p a_{ij} S_j \quad (1)$$

Here, p is the number of aerosol sources, C_i is the mass concentration of the i th elemental component of the sample in $\mu\text{g}/\text{m}^3$, a_{ij} is the fractional amount of component i in emissions from source j , and S_j is the amount of the aerosol mass concentration attributable to source j . S_j /(total sample mass concentration) is termed the source apportionment fraction. Apportionment of the source is achieved by measuring trace element component profiles of the aerosol sources, thus obtaining values for a_{ij} , analyzing the aerosol in the collected aerosol sample for the same components, and determining S_j using a least squares analysis of the overdetermined system of equations expressed by equation 1.

The CMB analysis used for the work employs effective variance weighting for the least squares calculation of the source apportionment terms S_j in equation 1.^{3,11} In this analysis the S_j are determined by minimizing the following chi-square (χ^2) function:

$$\chi^2 = \sum_i \frac{(C_i - \sum_j a_{ij} S_j)^2}{\sigma_c^2 + \sum_j \sigma_{a_{ij}}^2 S_j^2} \quad (2)$$

Here σ_c is the standard error in C_i , and σ_a is the standard error in a_{ij} . The minimization was carried out using a direct search technique rather than matrix inversion calculations.

RESULTS

Average values for the CMB source apportionments are given for mines E, F, and G in Table III for the fine, sub- $0.7 \mu\text{m}$, and coarse, super- $0.7 \mu\text{m}$, portions of the dichotomous samples. Errors quoted in the table are more indicative of the variability of the results from sample to sample than of the true statistical errors. In each case diesel exhaust is the dominant component of the submicron aerosol, greater than 92%. These apportionments deviate from those of the coal

Table II
Summary of Log-normal Size Distribution Parameters for Average Aerosol
Distributions Measured in Haulage Entries of Diesel Equipped
Metal and Nonmetal Mines

Mine	Submicron			Coarse		
	Mass mean dia. ¹ μm	Geometric std. dev. ² σg	Mode ³ conc. mg/m ³	Mass mean dia. ¹ μm	Geometric std. dev. ² σg	Mode conc. mg/m ³
D	0.18 ± 0.03	2.5 ± 0.2	0.6 ± 0.2	5.1 ± 1.0	3.1 ± 0.3	0.7 ± 0.2
E	0.16 ± 0.13	2.4 ± 0.7	0.20 ± 0.06	6.1 ± 3.3	1.8 ± 0.3	7.5 ± 4.0
F	0.26 ± 0.04	1.6 ± 0.1	1.4 ± 0.3	3.8 ± 0.7	2.4 ± 0.3	1.1 ± 0.8

¹ Mass Mean Diameter (MMD)

² Geometric Standard Deviation (σg)

³ Mode concentration

Table III
CMB Source Apportionment Results for Mines E, F, and G

Mine	Source	RESPIRABLE SIZE FRACTION, %	
		SUB-0.7 μm	SUPER-0.7 μm
D	Diesel	94 ± 12	25 ± 20
	Ore	5.6 ± 0.8	75 ± 13
E ¹	Diesel	95 ± 7	<20
	Ore	4.9 ± 4.8	81 ± 7
F	Diesel	92 ± 12	40 ± 5
	Ore	<12	60 ± 5

¹Gassy mine, wet scrubber used.

mine samples in that a significant fraction of the respirable coarse aerosol in the mines where diesel equipment does not use a wet scrubber is diesel—up to 40% for Mine F.³ This translates to approximately 20% of the total diesel aerosol being greater than 0.7 μm in size.

Applying modal analysis to concurrent size distribution samples permits a comparison with the CMB analysis results. Table IV gives this comparison for coarse particle contamination of the sub-0.7 μm aerosol in the three diesel equipped metal and nonmetal mines. The two analyses give the same result, within the quoted errors.

CONCLUSION

Using the results of the limited CMB analysis, two points can be made concerning the contribution of the various diesel mine sources to both fine and coarse fractions of the respirable aerosol concentrations in the metal and nonmetal mine environment:

1. Diesel exhaust aerosols are the dominant component of the submicron mode aerosol measured in the diesel

Table IV
Average Coarse Particle Contamination of Sub-0.7 μm
Samples for Mines E, F, and G

Mine	Analysis	
	Modal %	CMB %
D	4 ± 2	5.6 ± 0.8
E	<2	4.9 ± 4.8
F	2 ± 1	<12

mines. More than 90% of the measured aerosols is contributed from diesel sources.

2. As much as 20% of the diesel exhaust aerosol contributes directly to the coarse part of respirable aerosol in the mine atmosphere.

It is not clear that the size selective technique used in the measurement of coal mine diesel aerosol can be extended to diesel-equipped metal and nonmetal mines. That technique depends on separating the collected aerosol sample into two size fractions at $0.8 \mu\text{m}$.⁴ In metal and nonmetal mines the substantial contribution to the respirable coarse fraction made by diesel exhaust aerosol compromises the use of size selective sampling, reducing the accuracy to less than 80%. As a result, alternate, carbon-specific, methods for determining diesel aerosol concentrations should be used in such mines if higher accuracy is desired. One such method is thermal-evolved gas analysis.¹² This technique permits analysis of the volatile, carbonate, and elemental carbon fractions of an aerosol sample. It should permit an unambiguous analysis of elemental carbon (soot) in a mine aerosol sample.

REFERENCES

1. Marple V. A., Kittleson, D. B., Rubow, K. L., and Fang, C. P.: Methods for the Selective Sampling of Diesel Particulate in Mine Dust Aerosols. *BuMines UFR 44-87*, NTIS PB88-130810. Washington (1986).
2. McCawley, M.: Diesel Particulate Measurement Techniques Applied to Ventilation Control Strategies in Underground Coal Mines. *Ongoing BuMines contract No. JO 145006*. NIOSH, Morgantown, WV (1988).
3. Cantrell, B. K.: Source Apportionment Analysis Applied to Mine Dust Aerosols: Coal Dust and Diesel Emissions Aerosol Measurement. *Proc. 3rd Mine Vent. Symp.*, pp. 495-501. Soc. Mining Eng. State College, PA (1987).
4. Rubow, K. L., Marple, V. A., and Cantrell, B. K.: Measurement of Coal Dust and Diesel Exhaust Aerosols in Underground Mines. *Proceedings of the VIIIth International Pneumoconioses Conf.* NIOSH, et al. Pittsburgh, PA, (1988).
5. Mogan, J. P., Dainty, E. D. and Lawson, A.: Performance of Conventional and Advanced Water Scrubbers for Controlling Underground Diesel Exhaust Emissions. *Canadian Mineral and Energy Technology*. Mining Research Laboratories Division Report, M&ET/MRL 86-111,(OP,J). Quebec (1986).
6. Marple, V. A. and Rubow, K. L.: Respirable Dust Measurement. *BuMines OFR 92-85; NTIS PB 85-245843*, Washington (1984).
7. Lederer, C. M., Hollander, J. M. and Perlman, I.: *Table of Isotopes*, 6th Ed., p 58. John Wiley & Sons, New York (1967).
8. Rahn, K. A.: *The Chemical Composition of the Atmospheric Aerosol*. Technical Report, University of Rhode Island, Narragansett, RI (1976).
9. Whitby, K. T.: *Modeling of Atmospheric Aerosol Particle Size Distributions*. PTL Progress Report, U.S. EPA Grant No. R800971. Minneapolis, MN (1975).
10. Miller, M. S., Friedlander, S. K. and Hidy, G. M.: A Chemical Element Balance for the Pasadena Aerosol. *J. Colloid-Interface Sci.* 39:165-176 (1972).
11. Watson, J. G. Overview of Receptor Model Principles. *APCA J.* 34:619-623 (1984).
12. Malissa, H., Puxbaum, H. and Pell, E.: Zur Simultanen relativkonduktometrischen Kohlenstoff und Schwefelbestimmung in Staben. *S. Anal. Chem.* 109:109 (1976).

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MEASUREMENT OF AIRBORNE DIESEL PARTICULATE IN A COAL MINE USING LASER RAMAN SPECTROSCOPY

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INTRODUCTION

The goal of this research has been to develop the Laser Raman Quantitative Analysis (LRQA) method to measure the composition of respirable particulate, i.e. the fractions of coal and of diesel particulate, in the mine ambient air. In earlier Bureau of Mines sponsored research, we successfully demonstrated that the LRQA method could be used to measure the fraction of Diesel Particulate Matter (DPM) in coal/diesel particulate mixtures which were prepared in the laboratory.¹ The immediate objective was to test and refine this LRQA method on samples collected in a diesel underground coal mine.

Specific objectives required to meet this goal include:

1. Develop in-mine sample collection methods which will insure sufficient particulate loading on filters for LRQA.
2. Develop methodology for in-mine collection of reference samples ("coal-only" and "diesel-only" filters) which are required for quantitative LRQA.
3. Analyze precision and accuracy of the LRQA method.
4. Compare composition measurements with another analytical method, i.e. the University of Minnesota/Bureau of Mines size-selective sampling Micro-Orifice Uniform Deposit Impactor (MOUDI) method.

An advantage of the LRQA method is that it allows analysis of filters which have been collected by a method similar to that used to determine the respirable dust concentration in US underground coal mines. No new sampling instruments and techniques are required. Transfer of sample from collection substrate to analysis substrate is not necessary. Furthermore, other analyses can be made on the same sample since the technique is nondestructive.

The health effects of diesel exhaust, especially particulate, are a concern in the underground workplace. The constituents of DPM include insoluble carbonaceous particle agglomerates, adsorbed or condensed soluble organic compounds, trace metals, and low level sulfates. Many of the organic compounds are mutagenic and some are known carcinogens.^{2,3}

Measurements made in underground mines with diesel equipment have shown that DPM may contribute as much as 60 % of the 2.0 mg/m³ respirable coal mine dust standard.⁴ While coal dust has been an important health concern for a number of years, the concern about DPM is more recent.⁵

Measurement of pollutant concentrations is prerequisite to engineering control of the airborne particulate and gaseous pollutants to which a miner is exposed in a diesel underground coal mine. At the present time, there is no fully-proven quantitative analysis method which can distinguish between diesel and coal particulate.

EXPERIMENTAL

The mine air particulate samples were collected in a manner similar to that used for gravimetric respirable dust sampling in underground coal mines. Respirable dust was sampled using a personal sampler which draws mine air at 2 L/min through a 10 mm nylon preseparator and then through a filter at 2 L/min. Diesel/coal samples were collected in triplicate (collection times varied from 2.95 to 7.27 hr). Smaller Gelman A/E glass fiber particulate collection filters (25 mm filters instead of the normal 37 mm diameter) were used to assure filter loadings close to 0.10 mg/cm² and preferably 0.15 mg/cm². This 0.1 mg/cm² nominal level was determined by LRQA of various filter loadings above and below this level in previous studies. Only 8% of the samples fell below 0.07 mg/cm² with the majority falling in the 0.1 to 0.4 mg/cm² range (72%). Three locations were sampled for the diesel/coal mixtures each day: near the feeder-breaker, in the return, and on the ram car within 2 feet of the operator (as designated in Figure 1).

As part of a systematic approach to monitoring diesel emissions for control of mine air quality, we also measure ambient air pollutants and CO₂ concentrations.⁶ This approach, developed at Michigan Technological University (MTU), provides a means to relate air quality measurements to engineering controls. The CO₂ concentration, which is related to the fuel consumption and airflow per unit of diesel power used, is related to the DPM fraction. A typical value of 13 mg/m³ /%CO₂, determined from previous sampling in a number of metal mines, was used to calculate this CO₂-derived DPM value. The DPM concentration estimated using the % CO₂ does not compare well with LRQA values; % CO₂—is expected to be a rough indicator only.

Four "diesel-only" tailpipe particulate matter samples were collected from each of 3 Ram Cars using the portable Emissions Measurement Apparatus (EMA). The EMA, developed at MTU, is illustrated in Figure 2.¹ The EMA is a tailpipe apparatus designed to instantaneously and dynamically dilute the exhaust to a dilution ratio of about 20:1. A 63 mm

diameter Pallflex T60A20 filter was used to collect particulate (ca. 1.5 min sampling time).

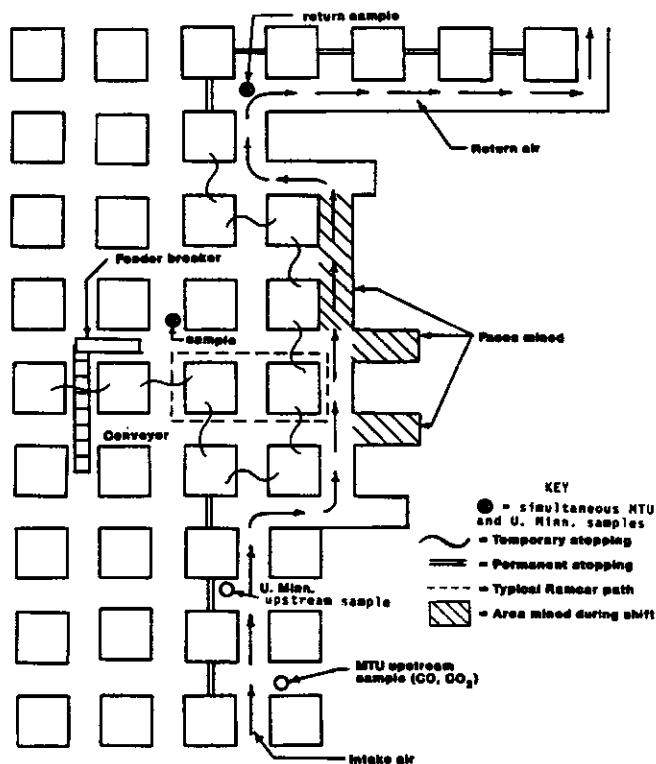


Figure 1. Schematic of coal mine section defining sampling locations.

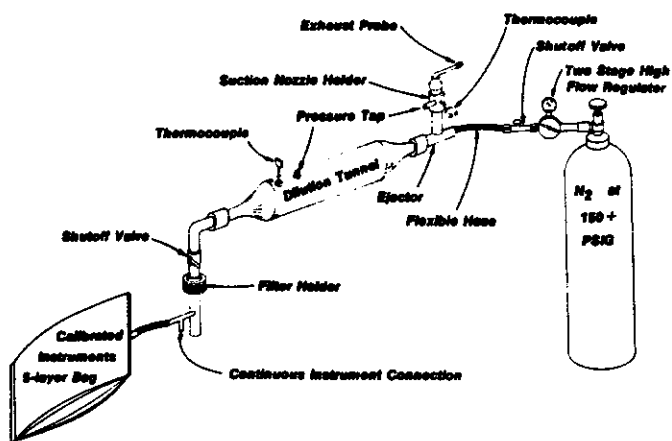


Figure 2. Schematic of emissions measurement apparatus (EMA-2) which is used to collect diesel-only tailpipe samples.

apparatus designed to instantaneously and dynamically dilute the exhaust to a dilution ratio of about 20:1. A 63 mm diameter Pallflex T60A20 filter was used to collect particulate (ca. 1.5 min sampling time).

“Coal-only” particulate reference samples were taken daily for 4 days next to the continuous miner (CM) scrubber (Figure 3). The collection procedure was similar to that used for the diesel/coal mixture samples. With the high dust concentrations between the cutter and scrubber, respirable coal dust can be collected in 15 minutes or less.

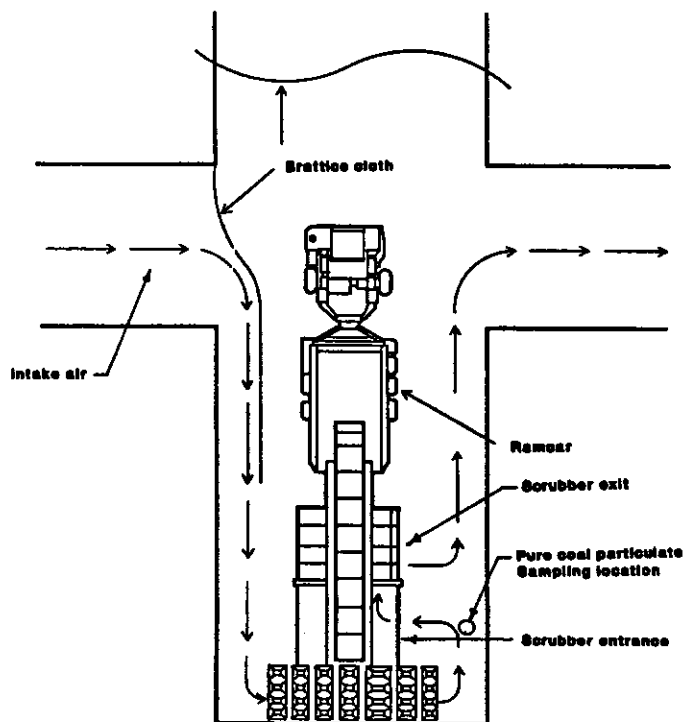


Figure 3. Illustration showing location of coal-only particulate sample collection.

After weighing to determine the respirable dust concentration, the filter is mounted on a sample spinner and analyzed by LRQA. No transfer of the particulate to a different filter is required. Samples are rotated to prevent decomposition in the laser beam.¹ The schematic in Figure 4 depicts the LRQA instrumentation.

The LRQA spectral scan procedures have been designed to test for sampling inconsistencies which might arise from sample decomposition in the laser beam. Four spectra are collected, a pair at each of two different radii on the spinning filter. The individual spectra are designated as “1x spectra.” The sum of the two spectra at one radius is designated as a “2x spectrum.” Any decomposition in the laser beam will

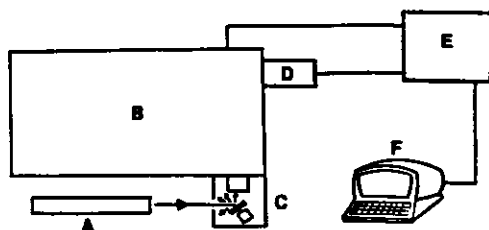


Figure 4. Schematic diagram of Raman instrumentation used to collect coal/diesel particulate spectra.

- A) Argon-ion laser
- B) Spectrometer (double monochromator)
- C) Sample chamber with spinning sample holder
- D) Photomultiplier tube
- E) Interface between spectrometer and computer
- F) Computer used to control spectrometer and to analyze spectra

be apparent upon comparison of two 1x spectra. Comparison of two 2x spectra will indicate radial inhomogeneity. This procedure also allowed detection of radial sampling inhomogeneities on a filter which are caused by particle size segregation. The sum of all four 1x spectra is designated as a "4x spectrum," and is representative of a given filter.

LRQA samples have been collected simultaneously with the size-selective sampling method being developed at the Twin Cities Research Center (TCRC) and the University of Minnesota.^{4,7} The latter samples were collected by University of Minnesota personnel. MOUDI samplers, used for this purpose, separate the particles into size fractions on the basis of their aerodynamic diameters and densities.⁷ This side by side collection allows direct comparison of the fractions of diesel and coal in the mine air measured by the two methods. All samples were collected during one week of underground air sampling during August, 1987, in the Kerr McGee Galatia Mine.

RESULTS AND DISCUSSION

Coal-only and Diesel-only Measurements and Use

A well defined relationship (equation 1) exists between the diesel/coal composition (y) and the intensity ratio (M) of two bands in the Raman spectrum of a mixture.¹ Figure 5 graphically depicts this relationship. Raman spectra of coal-only and diesel-only samples are shown in Figure 6.

$$1/y = (g'/g) \{ (r'-M)/(M-r) \} + 1 \quad (1)$$

y is the percent diesel particulate matter, %DPM, in a coal/DPM mixture. g represents the coal-only intensity and g' represents the DPM-only intensity. The slope in equation 1, g'/g , is the intensity ratio of the two samples and must be obtained when the two components are identically aligned. The coal-only intensity ratio (r) and the DPM-only ratio (r') must be determined to allow quantitative analysis of the mixtures.

The ratio for coal-only filters (r) was determined for 6 filters which were collected on three different days. The 1x, 2x and

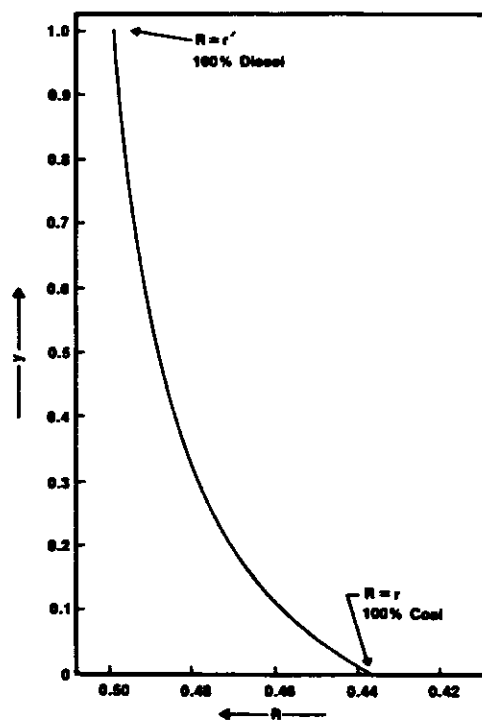


Figure 5. A graphical representation of the dependence of composition, i.e., %DPM (y), upon the experimental intensity ratio (R).

4x spectra demonstrate good reproducibility. This consistency shows that the samples are not decomposing in the laser beam. The mean and standard deviation (SDEV) for the coal-only samples are 0.522 and 0.022, respectively (C.V. = 4.3%). This precision is comparable to that expected theoretically for these scan times.¹ The overall accuracy of mixture composition analysis depends on precise measurement of the coal-only intensity ratio (r) and the DPM-only ratio (r').

Spectral ratios have been determined for four DPM-only filters (after-scrubber), collected from two different ram cars. A mean r' value has been calculated by averaging the ratios measured for the four filters (a pair collected from each ram car). Reproducibilities for these are reasonable with an average r' of 0.958 and with a SDEV of 0.089 (C.V. = 9.3%).

Spectral Analysis and Reproducibility

The calculated %DPM values are analyzed statistically to demonstrate spectral reproducibility for a triplicate set of filters. Table I summarizes the %DPM values for one set of diesel/coal mixture filters collected at the feeder-breaker. The %DPM for each filter in column B of Table I are each an arithmetic mean of four 1x spectra. Column C gives the corresponding standard deviations. At the bottom of this table the overall arithmetic mean and standard deviation for the 12 spectra are given. Column D presents the %DPM measured on the summed (4x) spectra, with the mean and

Table I
Statistical Analysis of %DPM for a Triplicate Set of Filters
Collected at the Feeder-Breaker (on 8/10/87)

Column:	B	C	D	F	G
	‡ DPM for four 1x spectra		‡ DPM for one 4x spectrum	‡ DPM for the 2x spectra	
Filter	Mean	SDEV		Inner	Outer
3393	60.4	9.3	65.9	55.6	70.9
4730	61.9	8.7	67.6	62.5	68.9
6337	67.7	8.4	61.7	57.1	65.9
Values for twelve 1x spectra: 63.3	8.8		Values for three 2x spectra, mean: 58.4	68.6	
Values for three 4x spectra: 64.9	3.0		and SDEV: 3.6	2.5	

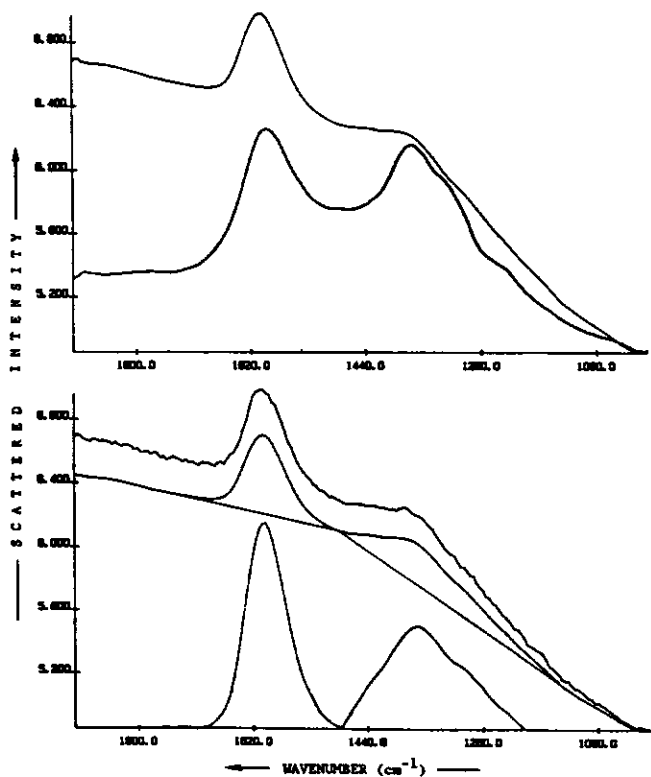


Figure 6. Raman spectra of coal-only and DPM-only filters (top), and baseline subtraction procedure for measurement of the intensity ratio (bottom).

standard deviation for the set of three at the bottom. Note that the standard deviation for the 4x spectra is smaller than for the 1x spectra because of the increased S/N ratio in each summed spectrum. The inter-filter mean composition is 64.9% DPM.

The intra-filter reproducibility is measured by the standard deviation of the %DPM (in column C of Table I) for each filter. The 4x %DPM for each filter (column D) must be consistent with the 1x average (column B), and they are in each case. These results indicate that the samples have not changed during the time of measurement in the laser beam.

Table I also compares %DPM values for 2x spectra (each a sum of two 1x spectra) collected at two different radii (columns F and G). This comparison shows whether or not the sample is radially homogeneous.

The inter-filter reproducibility is demonstrated by the standard deviation for the three filters (bottom of Table I, column C). In particular, the values in column D provide a measure of the inter-sample precision which can be attained for three filters collected simultaneously. The SDEV of 3.0% DPM demonstrates the high precision attainable. It is comparable to the uncertainty predicted theoretically upon consideration of standard counting statistics and the count time per data point. SDEV values that are higher than this will be found when real sampling differences occur.

Composition Measurements at the Feeder Breaker Ram Car, and Returns

Table II summarizes the DPM compositions at the various mine locations. While we have observed some inconsistencies for some filters, DPM compositions between 60 and 83% (SDEV < 10.5) have been measured with good precision. Samples with compositions outside this range exhibit inconsistencies among the multiple 1x spectra. Their origin is under further study.

In some filters the compositions measured at the two different radial positions differ substantially, as indicated by a t-test on the difference of the means (see Table II). Table III presents an example calculation. The null hypothesis that the two sets of data are equal can be rejected at the 95% confidence level if the t-value is greater than 2.9. We can reject the null hypothesis since the observed t-value is 6.4. This result indicates that the compositions measured at these two radii are statistically different. The inner radius has a higher coal content.

Five out of eleven of the filter sets listed in Table II show significant differences between the means for the 2x spectra at the inner and outer radii. These results indicate inhomogeneous deposition which changes the measured coal/diesel ratio. Visual observation also reveals the inhomogeneous particulate deposition on some filters. Therefore steps must be taken to insure uniform deposition.

Table II
Summary of %DPM and Statistical Results to Determine if
Inner Radius and Outer Radius Analyses Differ

Sample Location	Date taken	No.*	% DPM		C.V. %	Calc. t at		Inhomogeneous at 95% conf.	% DPM*** est. from CO ₂ conc.
			Mean**	SDEV**		t	0.05		
Feeder	8/10	3	64.9	3.0	4.6	3.8	2.9	yes	ND
	8/11	2	65.1	10.5	16.1	5.9	6.3	-	ND
	8/12	3	47.4	16.4	34.6	7.1	6.3	yes	68.8
	8/13	2	47.9	30.3	63.1	3.6	6.3	-	93.6
Ram Car	8/11	3	48.4	13.4	27.8	6.4	2.9	yes	47.2
	8/12	2	68.2	6.3	9.2	8.1	6.3	yes	65.1
	8/13	2	70.0	10.0	14.2	2.0	6.3	-	54.8
Return	8/10	2	77.9	0.6	0.7	2.0	6.3	-	78.9
	8/11	3	83.1	7.5	9.1	2.7	2.9	-	57.7
	8/12	2	82.4	7.9	9.6	3.0	6.3	-	49.9
	8/13	3	60.7	11.1	18.2	4.1	2.9	yes	59.7

* Number of samples analyzed per set.

** Mean and standard deviation for two or three 4x scans.

*** %DPM estimated from CO₂ concentration in mine.

Table III
Statistical Analysis of %DPM for a Triplicate Set of Filters with
Radial Inhomogeneity; Ram Car (8/11/87)

Column:	B		C		D		F		G	H
	% DPM for four 1x scans		% DPM for one 4x scan		% DPM for two 2x scans		Delta			
Filter	Mean	SDEV	Mean	SDEV	Inner	Outer	F-G			
2022	68.0	14.1	63.2		39.4	72.7	33.3			
2431	51.8	30.3	45.1		20.8	75.6	54.8			
6541	20.2	20.8	26.9		00.0	56.8	56.8			
Total number of spectra analyzed:	12		3		3		3		3	
Mean:	46.7		48.4		20.1		68.4		48.3	
SDEV:	31.5		13.4		19.7		10.2		13.0	
t :									6.4	

Segregation by particle size can cause such inhomogeneity, with the larger particle size coal particulate concentrated toward the center. This natural tendency for nonuniform deposition of particulate on the filter surface has been observed with asbestos fiber collection. Size-selective sampling research has indicated that coal dust tends to exhibit a particle size distribution above +0.7 micrometer with diesel particulate below 0.7 micrometer.^{4,7} Improved uniformity of particulate deposition has been achieved for asbestos fiber collection by using a cassette with a cylindrical "extension cowl." It should be pointed out that the observation of radial inhomogeneity demonstrates the sensitivity of the LRQA technique.

Comparison of Compositions as Measured by Different Methods

For two of three simultaneously collected samples there is excellent agreement between the MOUDI and the LRQA results (see 8/12 and 8/13 results in Table IV). The MOUDI

gives %DPM values of 46.2% and 62.1%, while the LRQA gives values of 47.4% and 60.7% DPM, respectively. For these two pairs, the overall time spans for collection were comparable and no sampling irregularities occurred. It is important to note that the Raman triplicate filters are collected at the same time and for the whole period (ca. 5 to 6 hr.), whereas the MOUDI samples are collected in sequence. Each MOUDI filter is collected over a 1 to 2.5 hr period. Thus the arithmetic mean %DPM values calculated by the two methods may differ because of the differences in times sampled. For the third measurement (on 8/11), the two methods do not exhibit such agreement. The mean values differ by 25%. During the last hour of sample collection on 8/11, the dust from the mine face did not pass by the samplers. This occurred when the continuous miner broke through the mine face into the adjacent drift, drastically changing the air flow pattern.

The S/N ratio based upon the counting statistics for the scan time used in this study indicates that precision is not limited

by the scan time. (A longer scan time will, of course, improve the S/N ratio.) Radial inhomogeneity reduces inter-filter reproducibility. Empirical variables can be controlled to improve precision. These are being optimized in our continuing work.

CONCLUSIONS

The LRQA method has been tested and refined on samples

collected in a diesel underground coal mine. The amounts of DPM found at the feeder-breaker, on the ram car or at the returns, are in the range from 37 to 83% DPM. Total respirable DPM ranges from 0.18 to 1.61 mg/m³ (Table V). Sampling reproducibility (precision) has been confirmed by statistical analysis of results for triplicate filters. Standard deviations below $\pm 10\%$ DPM are attainable. This precision is that expected for the scan conditions used. Reproducibility can be improved with longer scan times.

Table IV
Comparison of Compositions Measured by LRQA with those Measured by MOUDI and Those Estimated from %CO₂

Date/ Location	Sample No.	TIME			%DPM Est. from CO ₂ conc.	MOUDI			LRQA		
		start	stop	diff.		%DPM	Mean	SDEV	% DPM	Mean	SDEV
8/11/87 Return	GNA-1	10:19	11:19	60 min.*	47.1						
	GNA-2	11:41	12:41	60 min.+	51.7	57.9	14.84				
	GNA-3	13:01	14:01	60 min.++	74.8						
	20	8:20	14:00	5.76hr.	56.7			77.8			
	21	"	"	"	57.2			79.7	83.1	7.5	
	22	"	"	"	59.2			91.7			
8/12/87 Feeder	GNA-4	8:38	11:08	150 min.**	51.7						
	GNA-5	11:29	13:59	150 min.**	40.7	46.2	7.78				
	30	8:35	13:45	5.17 hr.	-			40.9			
	31	"	"	"	59.5			35.2	47.4	16.4	
	32	"	"	"	78.1			66.0			
8/13/87 Return	GNA-6	9:45	11:45	120 min.*	64.9						
	GNA-7	12:00	12:49	158 min.*	59.2	62.1	4.03				
			15:34	17:23							
	44	9:36***	17:15	4.87h	53.4			55.3			
	45	"	"	"	60.0			55.3	60.7	11.1	
	47	"	"	"	65.7			73.4			

+ some mining, moving mine roof bolting
++ dust from face not passing samplers
* mining
** hauling
*** pump off 12:51-15:38

Table V
Summary of LRQA %DPM, Total Respirable Dust and Airborne Diesel Particulate Matter

Sample Location	Date Taken	No.**	LRQA % DPM Mean*	Total Respirable Dust, mg/m ³	DPM mg/m ³
Feeder	8/10	3	65.1	0.915	0.596
	8/11	2	65.1	0.582	0.379
	8/12	2	47.4	0.596	0.283
	8/13	2	47.9	0.373	0.179
Ram Car	8/11	3	48.4	1.523	0.737
	8/12	2	68.2	1.158	0.790
	8/13	2	70.0	1.074	0.752
Return	8/10	2	77.9	1.073	0.836
	8/11	3	83.1	1.690	1.404
	8/12	2	82.4	1.957	1.613
	8/13	3	60.7	0.987	0.599

* Mean for two or three 4x scans.
** Number of samples analyzed per set.

Composition measurements for samples collected simultaneously and analyzed by the LRQA and size-selective methods have been compared. The %DPM values obtained for this limited set of samples at two locations are in reasonable agreement. Two out of three %DPM comparisons agree very well, the third does not.

Sampling objectives were attained which make quantitative Raman analysis possible. First, in-mine collection methods have been shown to provide satisfactory particulate loading on filters. Secondly, methods to provide the diesel-only and coal-only reference samples were developed.

We have demonstrated that sample homogeneity on the filter surface can be confirmed by scanning at two different radii. Filter "extension cowls" are expected to remove radial inhomogeneities, and these will be tested in up-coming work.

These results indicate the importance of DPM-monitoring techniques. Optimization of the LRQA procedures will allow increased precision and accuracy. Further comparison of the size-selective and the LRQA methods is needed. Improved monitoring methods that are able to quantify the diesel and coal fractions are prerequisite to the development of adequate control technology.

REFERENCES

1. Johnson, J.H., Carlson, D.H., Osborne, M.D., Reinbold, E.O., Cornilsen, B.C., and Lorprayoon, V.: *Monitoring and Control of Mine Air Diesel Pollutants: Tailpipe Emissions Measurements Aftertreatment*

Device Evaluation and Quantification of Diesel and Coal Fractions of Particulate Matter by Raman Spectroscopy. Annual Report to the United States Department of Interior, Bureau of Mines for Contract No. J0199125, Michigan Technological University, Houghton, Michigan 49931 (November 15, 1982).

2. Dainty, E.D., Mitchell, E.W., and Schnakenberg, Jr., G.H.: *Objectives and Achievements of a "Organization, Three-Government Collaborative Program on Diesel Emissions Reduction Research and Development", Heavy-Duty Diesel Emission Control; A Review of Technology*. CIM Special Volume 36 (1986).
3. French, I.W. and Mildon, M.A.: *Health Implications of Exposure of Underground Mine Workers to Diesel Exhaust Emissions—An Update*, 607 pp. CANMET, Energy, Mines and Resources, Canada, Contract No. Oust.82-00121 (April 1984).
4. Cantrell, B.K., Zeller, H.W., Williams, K.L. and Cocalis, J.: *Monitoring and Measurement of In-Mine Aerosol: Diesel Emissions*. pp. 18-40. USBM IC 9141 (1987).
5. Miner, G. M., Chairman: *Report of the Mine Safety and Health Administration Advisory Committee on Standards and Regulations for Diesel-Powered Equipment in Underground Coal Mines*. Report to the Secretary of Labor, U. S. Department of Labor, MSHA (July, 1988).
6. Johnson, J.H., Carlson, D.H., and Renders, C.F.: *Summary of Results of Diesel Mine Vehicle Emissions Control Research in MTU Mine Air Quality Laboratory*. Final Report to U.S. Department of Interior, Bureau of Mines for Contract J0145007, Michigan Technological University, Houghton, Michigan 49931 (February 15, 1987).
7. Cantrell, B.K.: *Source Apportionment Analysis Applied to Mine Dust Aerosols: Coal Dust and Diesel Emissions Aerosol Measurement*. Third U.S. Mine Ventilation Symposium, Penn State Univ. (Oct. 12-14, 1987).

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EXPERIMENTAL AND THEORETICAL MEASUREMENT OF THE AERODYNAMIC DIAMETER OF IRREGULAR SHAPED PARTICLES

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ABSTRACT

A theoretical technique has been developed and verified experimentally for determining the aerodynamic diameter of irregular shaped particles. The aerodynamic diameter of a particle is a very important parameter for determining where that particle deposits in the respiratory tract. Many instruments, such as impactors and cyclones, will determine the aerodynamic size distributions of aerosol particles but few analyze the particles individually. The theoretical approach of our technique is to solve, by use of high speed computers, the three-dimensional Navier-Stokes equations to obtain the flow field around an irregular shaped particle of any contour. The computer program will then determine the drag on the particle, and thus the aerodynamic diameter of the particle can be calculated. The experimental approach has been to pass the particles through a centrifuge and collect the particles upon a collection foil. The position of a particle on the foil is an indication of its aerodynamic diameter. These particles were then shadowed in two orthogonal directions and inspected under an scanning electron microscope (SEM). The top view of the particle in the SEM plus the views of the two orthogonal shadows allows one to determine the three-dimensional shape of the particle. Studies have been performed on silica, coal and talc particles with aerodynamic diameters in the 1 to 4 μm size range. The three-dimensional shape, as is determined from SEM analysis, was used in the theoretical computer program and the results compared. It was found that in most cases the agreement between the experimentally and theoretically determined aerodynamic diameters was within 5%.

INTRODUCTION

The equivalent aerodynamic diameter (EAD) of a particle, defined as the diameter of a unit density sphere with the same falling speed as the particle in question, is an important size measurement of the particle. This is especially true when attempting to predict where particles may deposit in the respirator tract. Therefore, EAD is an important parameter when considering respiratory diseases caused by particles, such as coal workers pneumoconiosis (CWP).

Many instruments will measure the EAD size distribution of the aerosol particles, but few analyze the particles individually. Impactors, cyclones and virtual impactors normally collect particles upon substrates or filters which are then analyzed gravimetrically to determine the mass concentration of the particles in that size classification. The EAD of particles can be measured on an individual basis with centrifuges, inertial spectrometers and the TSI Aerodynamic Particle Sizer (APS). Centrifuges are most ideally applicable for studying individual particles as the particles are deposited, on long removable foils, at locations dependent upon their EAD.

The theoretical approach to determining the EAD of a particle has been primarily limited to regular shaped particles of symmetry to which analytical solutions of the flow field equations for air flowing around the particles can be applied.

However, if the particle is irregular in shape, these analytical approaches do not apply and the EAD is very difficult to calculate. One technique that can be applied to determine the flow field around an irregular shaped particle is the numerical solution of the Navier-Stokes equations. In aerosol technology applications, this technique has been primarily used to determine the flow field through instruments. In most of these problems, the Navier-Stokes equations have only been expressed in two dimensions. However, to be able to describe the flow around any arbitrary irregular shaped particle, the Navier-Stokes equations must be solved in three dimensions.

The object of this paper is to apply the numerical solution of the three-dimensional Navier-Stokes equations to the flow around any irregular shaped particle and demonstrate that the aerodynamic diameter, so calculated, agrees with that determined experimentally in a centrifuge. Studies have been performed on silica, coal and talc particles with aerodynamic diameters in the 1 to 4 μm size range.

The shape of the particles used in the numerical solution of the flow field are defined by scanning electron microscopic (SEM) analysis of the particles collected on the foil in the centrifuge. An important discovery was made in the process of determining the three-dimensional shape of a particle in the SEM. It was found that the two-dimensional view of a particle is not sufficient to fully describe the shape of the

particle. To fully describe the particle, it is necessary to shadow the particle with a film in two orthogonal directions. These two shadows, along with the plane view of the particle, can then provide a reasonable indication of the particle shape.

NUMERICAL ANALYSIS TECHNIQUE

Numerical analysis of the Navier-Stokes equations has been used extensively in our laboratory to obtain information on flow fields through aerosol analyzing instruments.¹⁻³ Although several techniques have been used to solve the Navier-Stokes equations, they are all basically the same in that the finite difference form of the equation is expressed in terms of the stream function and vorticity, or in terms of the velocity vector components and the pressure. A grid is placed over the area of interest and the finite difference equations are solved at the node points (intersection of the grid lines) of the grid. The solution is achieved by an iterative relaxation procedure that determines the value of the stream function and vorticity or the velocity vector components and the pressure at each node point. Since numerical solution techniques have been used extensively and many cases reported in the literature,^{4,5} the techniques will not be described in detail here.

The particular numerical solution technique used in the work described here is that described by Patankar.⁴ The reader is referred to his textbook for details of the technique. This technique solves for the velocity vector components and the pressure at the node points rather than the stream function and vorticity. However, once the velocity vectors and pressure are known, the stream function and vorticity can be calculated, if desired. The stream function is often calculated so that the stream lines (lines of constant stream function) can be shown to provide a clearer understanding of the nature of the flow fields.

Most of the work utilizing finite difference solutions to the Navier-Stokes equations has been in two dimensions. However, three-dimensional solutions can be obtained⁶ and must be used when analyzing the flow around random irregular shaped particles. The solution technique is exactly as has been described by the two-dimensional analysis of Patankar, with the addition of the third direction. However, the computer program is substantially larger and the solution time much longer.

The fluid drag acting on the particle and the EAD can be computed from the numerically determined flow field surrounding the particle. Based on the calculated flow field, the fluid drag on the particle surface can be calculated by integrating the fluid stresses over the surface of the particle. The drag force on a particle will be the sum of both the pressure forces on the particle and the shear forces resulting from the fluid flowing past the surface of the particle. Once the drag force is equated to the gravitational force acting on a particle, the EAD is computed based on its basic definition. Since the aerodynamic diameter is defined as the diameter of a unit density sphere which falls at the same speed as the particle in question, the problem reduces to one of determining the falling speed of a particle. This problem further reduces to one of determining at what speed the drag

force is equal to the gravitational force on particle, for these are the conditions which must exist when the particle is falling in equilibrium at its terminal settling speed.

Verification of Numerical Technique on Regular Shaped Particles

Since two- and three-dimensional computer algorithms had not previously been applied to determining the flow around particles, the first step was to verify the programs on regular shaped particles where analytical solutions for the flow fields exist. The algorithms were therefore applied to particles that are symmetric in shape such as spheres, cylinders and disks. Due to symmetry, the drag acting on these types of particles can be computed as either two- or three-dimensional problems.

The two-dimensional program was verified by studying spheres, cylinders and disks.⁷ The two-dimensional analysis has been applied to single spherical particles, cylinders in cross flow, disk shape particles and spherical particles connected in chains. In all cases the shapes were selected because there was a prior determination of the drag force on the particle, either by analytical or experimental methods, and reported by other investigators, since it was the object of this portion of the project to gain confidence in a numerical technique. For the single spherical particle, the drag force from the numerical solution was compared to the drag force predicted by Stokes law. The results of this analysis for particle diameters of 2, 5 and 10 μm show that the calculation of the drag force on a particle agreed within 4% of that determined by Stokes law. For the case of cylinder in cross flow, which utilized rectangular coordinates, only one case was analyzed (10 μm diameter) and compared to the analytical solution. The difference was only approximately 2.5%. The disk in cross flow was studied utilizing cylindrical coordinates. The results of this test were compared to that of Oseen's solution. In the case of the disk, the analysis was run for several values of the Reynolds Number. The error in the drag forces increased with decreasing Reynolds Number from approximately 1 1/2% at a Reynolds Number of 0.13 to about 6% at a Reynolds Number of .00326.

Upon verification, the computational method was optimized and the technique expanded to include the three-dimensional case. For the three-dimensional case, test runs were performed on spherical and cubical particles. The numerically determined drag force on spheres was within 4.5% of the analytically determined value. For cubes, the values were within 5% of the experimental values reported in the literature.

Verification of Three-Dimensional Algorithms on Irregular Shaped Particles

The verification of the three-dimensional algorithm on regular shaped particles was encouraging. However, we felt that in the development of any numerical technique of this complexity, it is also important to compare the numerical results to experimental results, preferably obtained with a proven, standard method. For this reason a spiral duct centrifuge, which can provide information on the EAD of either regular or irregular shaped particles, was used to collect particles of several types. This instrument has been developed

and used successfully for many years by investigators to determine the EAD of agglomerates of spheres and chain aerosols as well as irregular shaped particles.^{8,9} In the centrifuge, particles are introduced into the center of a rotating spiral channel in which aerosol and clean sheath air are flowing. Particles introduced into the inner edge of the spiral channel are collected upon a foil attached to the outer edge of this channel. The distance from the introduction point to where the particles strike the foil is a function of their EAD, with the larger EAD particles being collected closest to the inlet.

The centrifuge used in this project was the Lovelace Aerosol Particle Separator (LAPS) which is used extensively by Lovelace Inhalation Toxicology Research Institute (ITRI). With the aid of ITRI personnel, several runs were made with coal, silica, and talc particles. This provided a variety of shapes for which the numerical technique could be applied. Sections from the centrifuge foils were removed at locations corresponding to aerodynamic diameters from 1 to 4 μm and the particles subjected to SEM analysis.

EXPERIMENTAL DETERMINATION OF PARTICLE SHAPE

The three-dimensional shape of an irregular shaped particle must be known in order to determine the EAD of the parti-

cle with the numerical computer program. However, inspection of the particles with the SEM only provides two-dimensional views of the particles. In our initial attempts to determine the three-dimensional shape of the particles, the shape and size of the particles in the third dimension were inferred from their two-dimensional shapes. This required that assumptions be made about the symmetry and regularity of the particles based on one two-dimensional view. It was realized that these assumptions could be erroneous. To eliminate the need for the assumptions in the third dimension, the particles were shadowed with a gold film in two orthogonal directions at an angle of 15° and then the particles and their shadows inspected with the SEM. The shadows were successful in providing views of the third dimension of the particles. This technique was very informative, in that the third dimensions of the particles were often drastically different than what we would have inferred from their two-dimensional shape. For example, a particle that looks like a sphere could in actually be a particle shaped like a disk or a spear.

Photomicrographs of four particles inspected in this manner are shown in Figure 1. These are three coal particles of various shapes and a talc particle. The particles in Figures 1a and 1b have projections protruding from the top of the particle. These projections would not have been suspected.

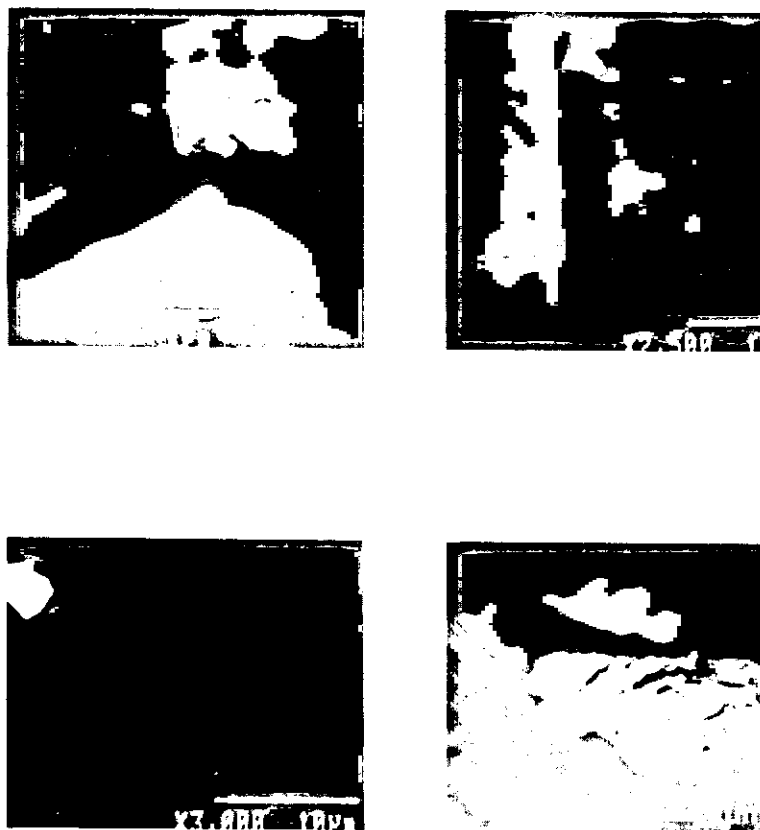


Figure 1. Photomicrographs of coal and talc particles shadowed in two orthogonal directions.

In some cases, the particles have multiple projections as shown in Figure 1c. The talc particle is a flakelike particle with a diameter approximately 10 times its thickness.

APPLICATION OF NUMERICAL TECHNIQUE TO CALCULATE AERODYNAMIC DIAMETER

The first step, in applying the numerical technique to determine the aerodynamic diameter of irregular shaped particles, such as shown in Figure 1, is to approximate the shape of the particles by a series of blocks as shown in Figure 2. The reason for approximating the particles as a series of blocks is that the numerical program is in rectangular coordinates and each cube in the three-dimensional array must represent either a portion of the particles or the space around the particles.

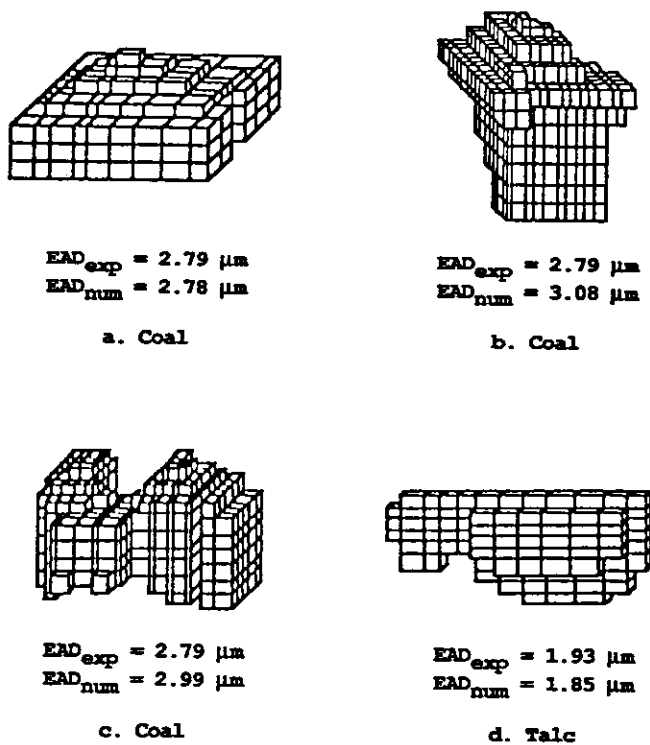


Figure 2. Digitized three-dimensional representations of particles in Figure 1 and a comparison of the numerically and experimentally determined EAD's.

Once the cubes within the three-dimensional array which represent a particle are identified, the viscosity in these cubes is set at a very high value. Therefore, when the flow field equations are solved over the entire domain (the domain of the particle plus the surrounding volume of approximately 10 times the particle diameter), the volume defined by the large viscosity will be considered as a solid within the domain and will not flow, while the volume around the particle will have the viscosity of air and will define the flow field around the particle. After the flow field has been determined, the drag on the particle can be calculated and, thus, its EAD

determined. For each particle shown in Figure 2, the experimentally determined EAD from the centrifuge is compared to the numerical results. In most cases the agreement is quite good, especially since the orientation of the particle as it passes from the inlet to the foil in the centrifuge is not known. The aerodynamic diameter of the particle will be a function of its orientation as it moves toward the foil.

To determine the sensitivity of a particle's aerodynamic diameter to its orientation, the aerodynamic diameter in three orthogonal directions were determined numerically for two particles shown in Figure 3. The table associated with each particle indicate that the aerodynamic diameter is a function of its orientation. Note that the variation is only about 17% from their smallest to largest value of EAD's. Also, indicated

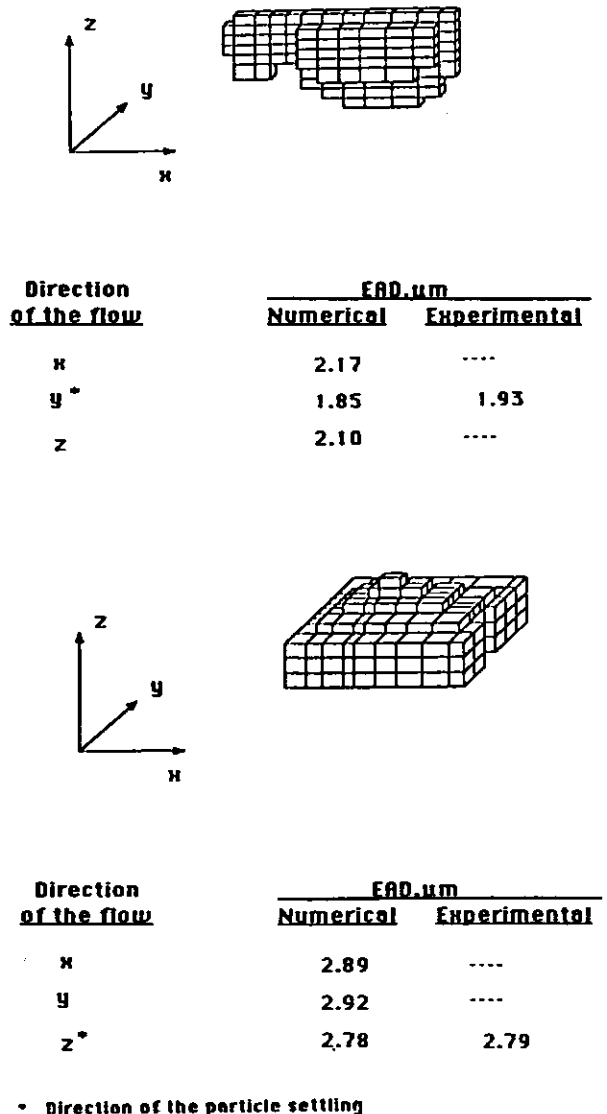


Figure 3. Comparison of the numerically determined EAD's for three orthogonal orientations of a talc and coal particle.

in the table is the experimentally determined EAD corresponding to the direction that the particle was found on the foil. The agreement between these experimental values of the EAD's and the theoretical EAD's for the same orientation is very good.

CONCLUSIONS

A powerful tool has been developed for determining the EAD of an irregular shaped particle in any orientation. This technique utilizes the numerical solution of the Navier-Stokes equations in three dimensions and provides detail for the features of the flow around the particle, which leads to the calculations of the drag coefficient and EAD of the particle. The experimental verification of the theoretical technique has been quite satisfactory in that the aerodynamic diameter determined experimentally agreed with the theoretically determined values.

In the process of determining the three-dimensional shape of a particle in an SEM, it was found that the shadowing of the particle in two orthogonal directions was necessary. This shadowing revealed that inferring the three-dimensional shape of a particle from its two-dimensional projection is not satisfactory and that the shadowing is absolutely necessary if detailed information of the particle shape and size is to be obtained.

REFERENCES

1. Marple, V.A.: A Fundamental Study of Inertial Impaction. *Ph.D. Thesis* University of Minnesota (1970).

2. Rader, D.J., Marple, V.A.: Effect of UltraStokesian Drag and Particle Interception on Impaction Characteristics. *Aerosol Sci. Technol.* 4:141-156 (1985).
3. Rader, D.J., Marple, V.A.: A Study of the Effects of Anisokinetic Sampling. *Aerosol Sci. and Technol.* 8:283-299 (1988).
4. Patankar, S.V.: *Numerical Heat Transfer and Fluid Flow*. McGraw-Hill-Hemisphere Publication, New York (1979).
5. Gousman, A.D., Pun, W.M., Runchal, A.K., Spalding, D.B., Wolfshtein, M.: *Heat and Mass Transfer in Recirculating Flows*, Academic Press, New York (1969).
6. Marple, V.A., Rader, D.J.: Recent Developments in the Application of Finite Difference Solutions to the Study of Flow Fields and Particle Trajectories. Presented at the *Third Symposium on Advances in Particle Sampling and Measurement* held in Daytona Beach, Florida (October 18-21, 1982).
7. Marple, V.A., Zhiqun, Z., Liu, B.Y.H.: Numerical Technique for Calculating the Equivalent Aerodynamic Diameter of Particles. Presented at *International Symposium on Respirable Dust in the Mineral Industries*, University Park, Pennsylvania (October 14-16, 1986).
8. Stober, W., Flachsbarth, H.: Size-Separating Precipitation of Aerosols in a Spinning Spiral Duct. *Environ. Sci. Technol.* 3:1280-1296 (1969).
9. Kotrappa, P., Light, M.E.: Design and Performance of the Lovelace Aerosol Particle Separator. *Rev. Sci. Instru.* 43:1106-1112 (1972).

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CHEMICAL SPECIATION AND MORPHOLOGICAL ANALYSIS OF RESPIRABLE DUST IN FOUNDRIES

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Various studies have related dust exposure of foundry workers to mixed-dust fibrosis,¹⁻⁴ bronchial obstruction,⁵ and lung cancer.⁶ The relationship between silicosis and pulmonary cancer has been constantly mentioned in the last ten years⁷⁻⁹ leading to the inclusion of silica in the IARC list of compounds which should be regarded as probably carcinogenic to humans.¹⁰ However, many of the epidemiological studies^{6-8,11,12} have indicated the almost impossible task of establishing a dose-effect relationship in foundries because of the complexity of workers' exposure, and the lack of data on cumulative exposure to etiologic agents.

The aim of this work was thus to selectively collect foundry dust with granulometric fractions of biological significance and to carry out a comprehensive analysis of these fractions.

Methods

Dust samples were collected at fixed stations with cascade impactors, cyclones and closed cassettes in three ferrous foundries, one aluminum foundry and one copper smelter.

Dust characterizations were performed by scanning and transmission electron microscopes fitted with energy dispersive X-ray analyzers (EDXA); X-ray photoelectron spectroscopy (ESCA), secondary ion mass spectrometry (SIMS), X-ray diffractometry, infrared spectrophotometry and atomic absorption spectroscopy.

Results

The melting technique, size of the industry, variety of compositions and whether the installation has dust control equipment are obviously highly related to the observed changes in dust composition. However, in this short presentation, results that are thought to be relevant to the toxicity of these dusts will be emphasized.

Ferrous foundries

The three ferrous foundries (A, B and C) cast ductile iron and gray brass in various types of sand moulds without any organic resins. Figure 1 gives a representative example of

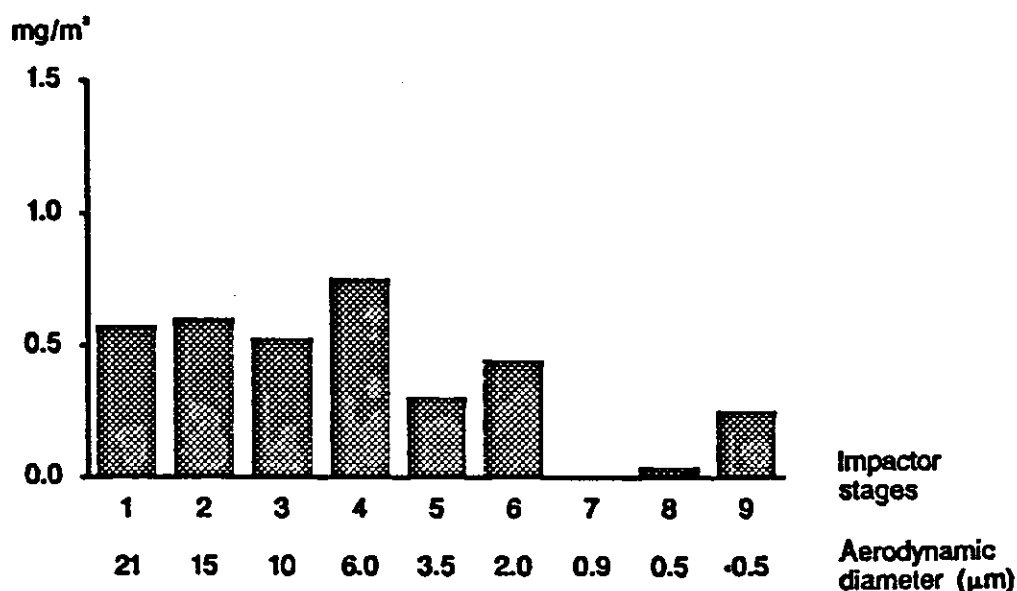


Figure 1. Example of the bimodal distribution of foundry dust as collected with a Sierra Cascade Impactor.

the bimodal distribution of foundry dust as particulate dust ($> 2 \mu\text{m}$) and fumes ($< 0.5 \mu\text{m}$) as observed by Dams and Zhang.¹³⁻¹⁴

In this instance, the dust concentration results as sampled with the cascade impactors in the general environment of the casting facility of each foundry can be conveniently separated into three fractions, each fraction being the sum of three successive impactor stages. The average dust concentrations can then be summarized as being 1.7, 1.5 and 1.6 mg/m^3 for particles having aerodynamic diameters larger than 10 μm ; 1.3, 2.5 and 0.8 mg/m^3 for particles between 1–10 μm ; and 0.3, 2.9 and 0.1 for particles smaller than 1 μm which we will describe as fumes. The striking feature of these results is the comparability of large-particle dust concentrations in the three foundries as compared to the variability of respirable dust and fume concentrations.

The determination of the quartz content of these foundries dusts gives a partial evaluation of their pulmonary toxicity. However, it was observed that the airborne quartz concentrations as sampled with the cascade impactor were 0.08, 0.10 and 0.08 mg/m^3 for particles in the 1–10 μm range, as compared to results of 0.04, 0.05 and 0.01 mg/m^3 as sampled with a standard cyclone for respirable dust. These results can be explained by the absence of quartz in the fume fraction or by the widening of the quartz diffraction line with the decrease in particle size which makes quartz unobservable.

The metallic elements detected in the airborne dust from ferrous foundries are given in Table I in decreasing order of intensity for particles larger or smaller than 1 μm . It is easily seen that the composition of particulates larger than 1 μm is much simpler than that of the fume portion of the aerosol. In contrast to the two other foundries, in foundry B there are significant proportions of lead in the portion of the aerosol composed of particles smaller than 1 μm . Foundry B was the only one melting untreated iron scrap. Elevated lead levels in the blood of scrap metal shop workers have been reported.¹⁴

Al foundry

The concentrations of dust particles at the Al foundry ranged from 0.6 ($> 10 \mu\text{m}$), 0.4 (1–10 μm) and 0.5 ($< 1 \mu\text{m}$) mg/m^3 . The sampling of total inspirable dust with a closed 35 mm—cassette gave an average of $2.6 \pm 0.9 \text{ mg}/\text{m}^3$ while respirable dust sampling with a cyclone gave an average of $1.1 \pm 0.3 \text{ mg}/\text{m}^3$. The analysis of these samples by SIMS, EDXA and ESCA showed a preponderance of NaF on all granulometric fractions with Cl and traces of Zn, and of Mn in particles smaller than 1 μm . Sodium fluoride is a respiratory tract irritant and a cause of fluorosis. The time weighted average concentration for worker exposure has been fixed at 2.5 mg/m^3 as F in the United States.

Cu smelter

Dust concentrations at the reactor and the converter stages of the smelting process were determined. Cascade impactors gave 1.0, 0.3 and 0.45 mg/m^3 for the three same fractions of large particles ($> 10 \mu\text{m}$), respirable particles (1–10 μm) and fumes ($< 1 \mu\text{m}$). For comparison purposes, inspirable dust as sampled with 35 mm closed cassette showed an average concentration of 2.6 mg/m^3 and respirable dust sampled with a cyclone was 1.0 mg/m^3 .

Quartz, As, Pb and Cu concentrations were compared to TLV^R values to infer a preliminary evaluation of the pulmonary aggressivity of these samples. Thus, the As, Pb and Cu concentrations of inhalable dusts were respectively 0.02, 0.23 and 0.26 as compared to the accepted TLV^R of 0.05, 0.15 and 1.0 (fumes: 0.2) mg/m^3 .

After extensive characterization by X-ray diffractometry and infrared spectroscopy, it was concluded that most of the lead was present as lead sulphate. The quartz concentration in respirable dust was around 5% as opposed to the 20–30% found in the flux.

In this industry, Fe, Cu and Zn are in general important and constant constituents of all particulate sizes, with lead being

Table I
Principal Elements in Foundry Dust as Measured by Secondary Ion
Mass Spectrometry and Photoelectron Spectroscopy

Foundries	Particle size μm	Elements (Decreasing order of intensity)
A and C	> 1	Ca, Fe, Zr, F, Zn
	< 1	Mn, Fe, Zn, Cu, Pb, Co, Cr, As, V
B	> 1	Ca, Fe, F, Zn
	< 1	Pb, Fe, Mn, Cu, Zn

Traces of Co, Cr, As, V.

Table II
Principal Elements in Dust from a Cu Smelter as Measured by Secondary Ion Mass Spectrometry (SIMS) and Photoelectron Spectroscopy (ESCA)

Instruments	Particle size μm	Elements (Decreasing order of intensity)
Both	> 1	Fe, Cu, Zn (Pb)
Both	< 1	Pb, Fe, Cu, Zn, S, Sn
SIMS	< 1	Br, Ba, In, Sr
ESCA	< 1	Cd, Se

present in particles smaller than 1 μm . The presence of lead in the fume portion of the dust was similarly noted in ferrous foundries. In, Cd, Se and of Sn are also observed in fume particles as well as traces of Ni, V, Cr and As.

Conclusion

A first step has been made in the comprehensive analysis of dust in foundries indicating the following trend: foundry dust can be conveniently separated into three fractions of particles sizes closely associated with inhalable particles (> 10 μm) respirable dust (1–10 μm) and fumes (< 1 μm). The present of lead compounds is largely concentrated in the fume fractions. The presence of quartz is detected in the inhalable and respirable fractions.

References

- Oudiz, J. Silica Exposure Levels in United States Foundries. *Silica, Silicosis and Cancer*. Edited by Goldsmith, D.F., Winn, D.M., Shy, C.M., pp. 21–28 (1986).
- Parkes, W.R. *Occupational Lung Disorders*, 2nd Edition, pp. 138 and 158–159 (1982).
- Pintar, K., Funahashi, A., Siegesmund, K.A. A Diffuse Form of Pulmonary Silicosis in Foundry Workers. *Arch. Pathol. Lab. Med.* 100:535–538 (1976).
- Ehrlich, R.I., Gerston, K.F., Lalloo, U.G. Accelerated Silicosis in a Foundry Shotblaster. *S. Afr. Med. J.* 73:128–130 (1987).
- Karava, R., Hernberg, S., Koskela, R.S., Luoma, K. Prevalence of Pneumoconiosis and Chronic Bronchitis in Foundry Workers. *Scand. J. Work, Environ. Health*, 2:64–72 (1976).
- Tola, S., Koskela, R.S., Hernberg, S., Jarvinen, E. Lung Cancer Mortality Among Iron Foundry Workers. *J. Occup. Med.* 21:753–760 (1979).
- Mirer, F., Silverstein, M., Maizlish, N., Park, R., Silverstein, B., Brodsky, L. Dust Measurements and Cancer Mortality at a Ferrous Foundry. *Silica, Silicosis and Cancer*. Edited by Goldsmith, D.F., Winn, D.M., Shy, C.M., pp. 29–44 (1986).
- Palmer, W.G., Scott, W.D. Factors Affecting the Lung Cancer Incidence in Foundrymen. *Silica, Silicosis and Cancer*. Edited by Goldsmith, D.F., Winn, D.M., Shy, C.M., pp. 45–56 (1986).
- Mattangelo, G., Zambon, P., Simonato, L., Rizzi, P. A Case-referent Study Investigating the Relationship between Exposure to Silica Dust and Lung Cancer. *Int. Arch. Occup. Health* 60:299–302 (1988).
- International Agency for Research on Cancer. Silica and some Silicates. In: *IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans*. Vol. 42 (1987 a).
- Low, I., Mitchell, E. Respiratory Disease in Foundry Workers. *Br. J. Ind. Med.* 42:101–105 (1985).
- Johnson, A., Chan-Yeung, M., Maclean, L., Atkins, E., Dybuncio, A., Cheng, F., Enarson, D. Respiratory Abnormalities among Workers in an Iron and Steel Foundry. *Br. J. Ind. Med.* 42:94–100 (1985).
- Zhang, J., Billiet, J., Dams, R. Elementals Composition and Source Investigation of Particulates Suspended in the Air of an Iron Foundry. *Sci. Total Environ.* 41:13–28 (1985).
- Dams, R., Zhang, Y. Elemental Composition of Dust in an Iron Foundry as Determined by Instrumental Neutron Activation Analysis. *J. Radioanal. Nuclear Chem.* 110 (2):305–320 (1987).
- Tola, S. Occupational Lead Exposure in Finland. III. Lead Scrap Smelties and Scrap Metal Shops. *Work, Environ. Health* 11 (2):114–117 (1974).
- Documentation of the Threshold Limit Values*, Fourth Edition. American Conference of Governmental Hygienists, Cincinnati, OH, pp. 195–196 (1984).

AQUEOUS SEDIMENTATION AND GLOVE BOX AEROSOL DETERMINATION OF POTENTIAL RESPIRABLE FIBERS FROM SAND SAMPLES USING SCANNING ELECTRON MICROSCOPY

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ABSTRACT

There is no established method which allows simple prediction of the aerosolized respirable particulate concentration from a compact sample such as sand, soil, crushed stone, etc. In response to a problem requiring such information, we have developed a simple method which we propose for further testing.

Ten grams of sample is suspended in 60 ml of filtered water in a 100 ml graduated cylinder, mixed by repeated inversion for 1 minute, and allowed to settle. Small (50–400 μ l) micropipette aliquots from a constant distance (0.5 cm) below the surface are taken at 2, 5, 15, 30 and 60 min and filtered onto 0.2 μ m pore membrane filters. The filters are attached to carbon and carbon coated, followed by standard quantitative analysis of fibers (and non-fibers, if indicated) using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA). For correlation, aerosol filter samples are taken in a glove box during or after pouring or mixing the sample. Results are expressed as fibers/gm of initial sample, or as fibers/ml in aerosol samples. As an example, sand samples tested contained 10^8 to 10^9 total particles/gm, 10^5 to 10^6 fibers $> 5 \mu$ m length/gm and 0.3 to 6 fibers/ml in aerosols. In the glove box conditions, the fraction actually aerosolized is approximately 1% of the total possible. Aerosol concentrations in rooms of varying volume can be predicted.

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